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PATENTS ABSTRACTS OF JAPAN, vol. 6, no. 231(C-  
135)(1109), 17th November 1982  
PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 7(C-  
144)(1152), 12th January 1983

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**EP 0 115 948 B1**

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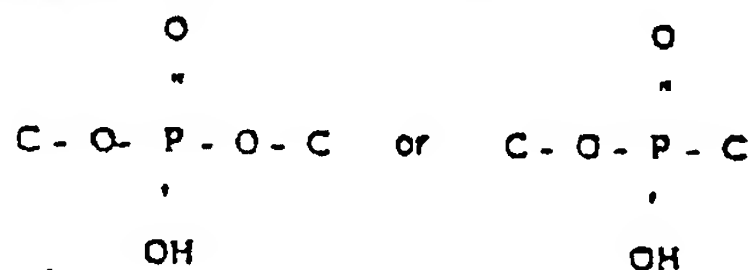
## Description

This invention relates to adhesive compositions that adhere strongly to any of the hard tissues of the living body, such as teeth and bones, metallic materials, organic polymers and ceramics, and whose adhesive strength has good water resistance. The term "adhesive compositions" as herein used not only means compositions used for bonding two or more adherends to one another, but also means compositions used for forming highly adhesive coatings on the surfaces of adherends such as metallic materials and organic polymers, and compositions used for forming highly adhesive fillings in the repair of hard tissues of the living body. In other words, the adhesive compositions to which this invention relates comprehend all compositions that exhibit adhesion to and thus are applicable to various kinds of substances, such as the hard tissues of the living body, metallic materials, organic polymers and ceramics.

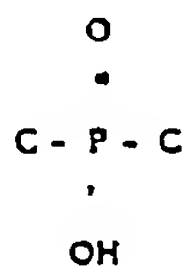
Various kinds of metallic materials, organic polymers and ceramics are used for the restoration of teeth. When these restorative materials are mounted in the mouth, it is necessary to ensure the adhesion between the teeth and the metal, organic polymer or ceramic and also the adhesion of the restorative materials to each other, for example, metal to metal, ceramics or organic polymer. In particular, since dentistry involves use in the mouth, the adhesion must be satisfactory under wet conditions.

Numerous and varied attempts to use phosphate compounds in adhesive compositions have already been made in the dentistry field.

(1) U.S. Patents Nos. 4,259,075, 4,259,117 and 4,388,043 indicate that a polymerizable composition containing a vinyl compound having a group of the formula:



is effective as a dental adhesive. U.S. Patent No. 4,222,780 indicates that a polymerizable composition containing a vinyl compound having a group of the formula:



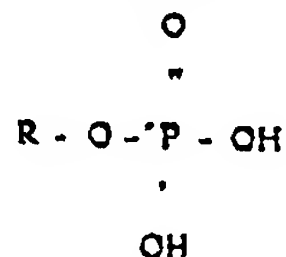
is an effective dental adhesive. Some of the compositions falling within the above patents have been widely used as primers for coating the cavity wall before a tooth cavity is filled. However, there were the problems that the cavity wall must be acid-etched beforehand in order to provide satisfactory adhesive strength to the tooth and that the adhesive strength to a Ni-Cr alloy commonly used in dentistry was not satisfactory.

(2) Attempts to obtain adhesives having adhesion to teeth using polymerizable phosphate compounds have also been made, e. g.

(i) U.S. Patent No. 3,882,600 describes phosphoryl monofluoride:

(ii) Journal of Dental Research, vol. 53, p. 878-888 and vol. 58, p. 943-952, Chemical Abstract, vol. 77, p. 290 (66 175 g) and Japanese Patent Application Laid-open No. 44152/1978 describe  $\text{CH}_2=\text{CH}-\text{PO}(\text{OH})_2$  and  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{PO}(\text{OH})_2$ :

(iii) Japanese Laid-open Patent Application No. 113843/1978 shows compounds obtained by neutralizing one of the two hydroxyl groups in compounds of the formula:

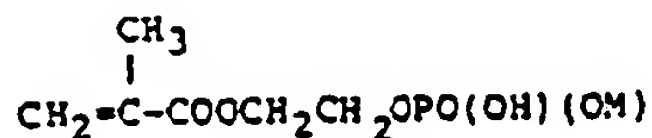


where R represents an organic residue having at least one vinyl group, specific examples of which include the following (where M represents an alkali metal):

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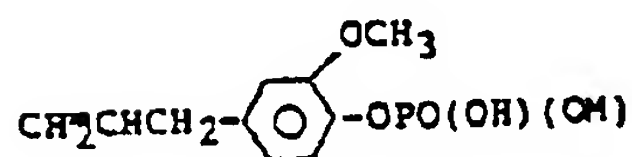
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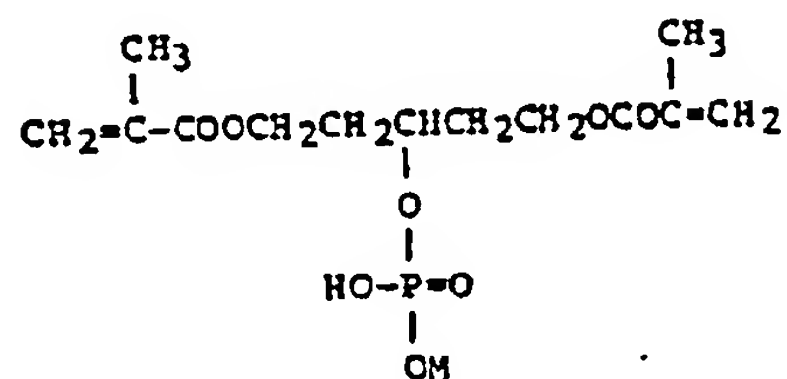
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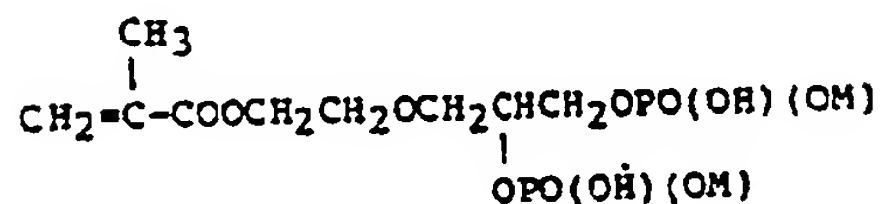


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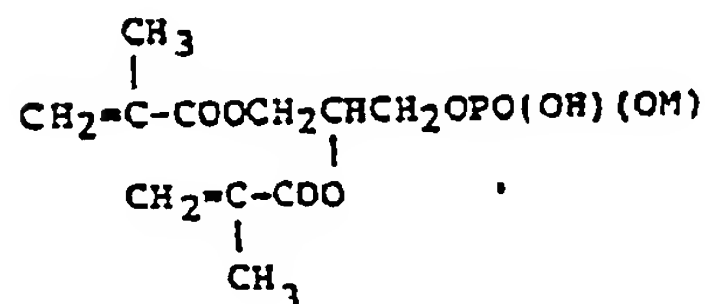
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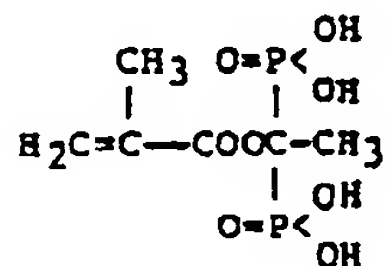
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(iv) Japanese Patent Publication No. 49557/1982 describes methacryloyloxyethane-1,1-diphosphonic acid of the following formula:

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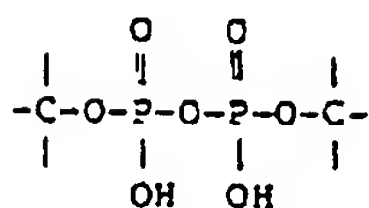
as an adhesive component in a dental adhesive.

In the case of all the compounds described in (i) to (iv) above, high adhesive strength (especially to metals) under wet conditions cannot be obtained.

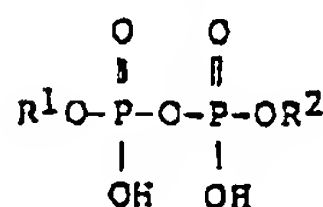
Japanese Laid-open Patent Specifications Nos. 131799/1982 and 18471/1982 disclose as a component of dental adhesive a pyrophosphate derivative having a polymerizable functional group and a group

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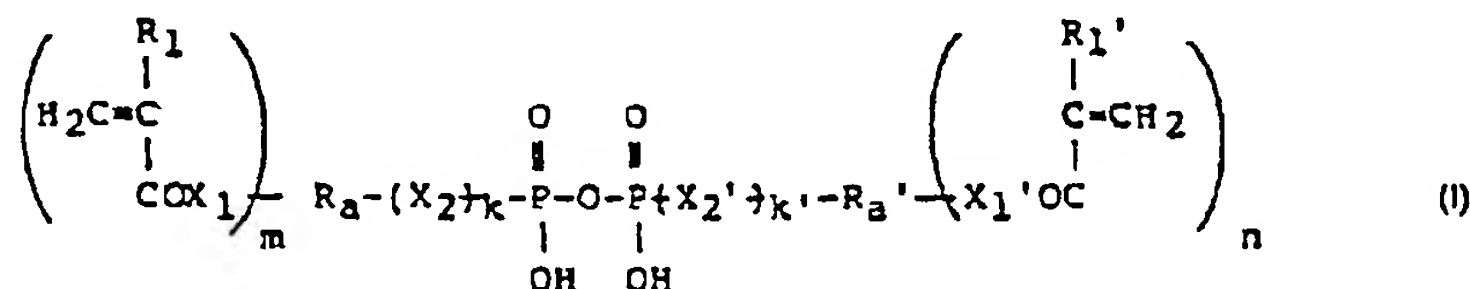
or preferably a pyrophosphate derivative of the formula



where  $\text{R}^1$  is an allyl, methacryloyloxy-( $\text{C}_{1-4}$  alkyl) or dimethacryloyloxy ( $\text{C}_{1-4}$  alkyl) radical; and  $\text{R}^2$  is an allyl, methacryloyloxy ( $\text{C}_{1-4}$  alkyl) or aryl radical and the  $\text{C}_{1-4}$  alkyl residue in  $\text{R}^1$  and  $\text{R}^2$  is optionally hydroxysubstituted. These specifications assert that these compounds increase the adhesive force for the enamel of human teeth, but they do not mention anything about adhesion to metals and further studies have in fact shown that the compounds do not significantly increase the water resistance of the adhesive strength for metals.

Further, attempts to use phosphate compounds in adhesive compositions have been made widely in various industries. Examples are disclosed in U.S. Patents Nos. 3,754,972, 3,884,864, 3,987,127, 4,001,150, 4,044,044, 4,223,115, Japanese Laid-open Patent Applications Nos. 20238/1974, 100596/1975, 125182/1978, 12995/1978, 11920/1981 and 44638/1982, and Japanese Patent Publication Nos. 4126/1980, 4790/1980. However, none of the phosphate compounds described in the above patent literature is free from problems associated with the retention of adhesive strength in the presence of water.

The present invention provides an adhesive comprising (a) 1 part by weight of a compound represented by the formula



in which each

$\text{R}_1$  and  $\text{R}_1'$  is a hydrogen atom or a methyl group, each of  $\text{X}_1$ ,  $\text{X}_1'$ ,  $\text{X}_2$  and  $\text{X}_2'$  is O, S, or  $\text{NR}^*$ , where  $\text{R}^*$  is a hydrogen atom or a  $\text{C}_{1-4}$  alkyl group.

$m$  is 1, 2, 3 or 4,

$n$  is 0, 1, 2, 3 or 4, each of

$k$  and  $k'$  is 0 or 1,

$\text{R}_a$  is a  $\text{C}_{3-10}$  organic residue having a valency of  $(m+1)$ , and

$\text{R}_a'$  is a  $\text{C}_{1-10}$  organic residue having a valency of  $(n+1)$ ; and

(b) 0 to 199 parts by weight of a monomer that is copolymerizable with the compound (I).

The above-mentioned compound (I), on polymerization, exhibits adhesive properties for the hard tissues of the living body, metals, and ceramics. (This monomer may be referred to as the adhesive monomer hereinafter).

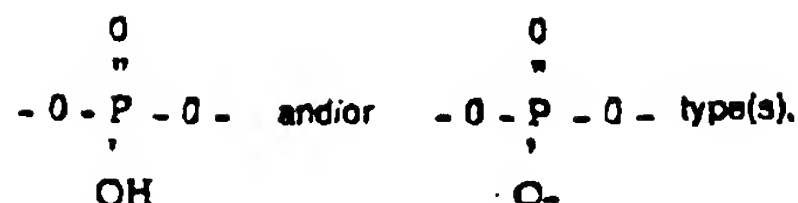
Compositions of the present invention can be used for bonding a hard tissue of the living body with another such tissue or a material for restoring the tissue (for example, a metal, an organic polymer or a ceramic material), or for filling and restoring such a hard tissue (e.g. a tooth), for coating the inside of a cavity of a tooth before filling, for bonding and fixing a tooth and a dental restorative material (e.g. inlay, onlay, abutment tooth, bridge, post, splint, orthodontic bracket or crown), for bonding dental restorative materials to each other (e.g. abutment tooth and crown), as a pit and fissure sealant for coating a tooth surface to prevent caries, for bonding metals, organic polymers and ceramics, or as adhesives in coating agents or paints to form a coating having excellent adhesion on the surface of a metal or a ceramic material.

The term "organic residue" means:

(i) a hydrocarbon group optionally containing OH, COOH,  $\text{NH}_2$  or halogen as a substituent; and

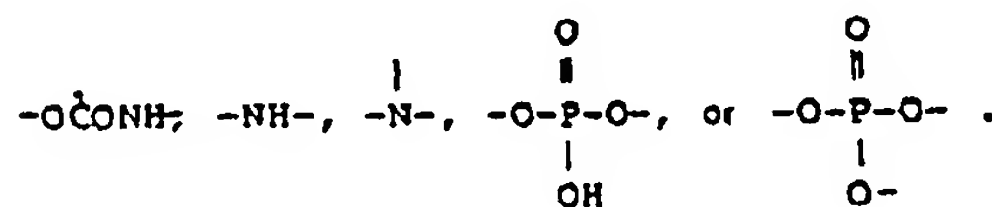
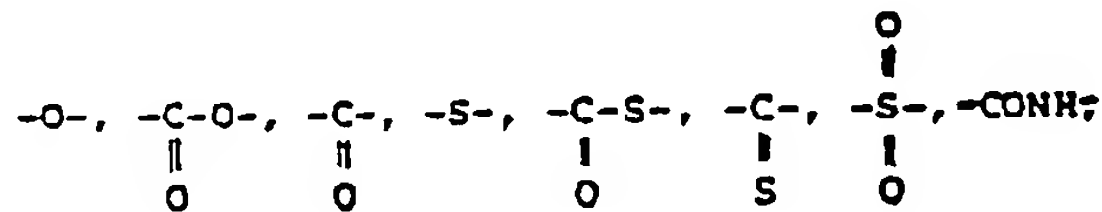
(ii) a group composed of 2 to 20 hydrocarbon groups of the type defined in (i) above connected to one another by linkages of one or more of the ether, thioether, ester, thioester, thiocarbonyl, amide, carbonyl, sulphonyl, urethane,  $-\text{NH}-$ ,  $-\text{N}-$ .

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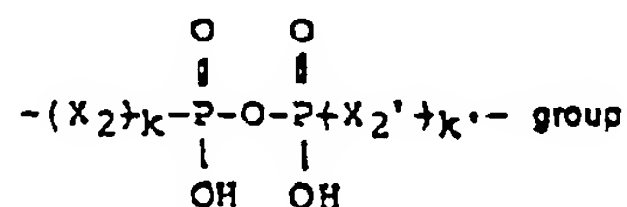


including not only those groups in which the main chain is made up of hydrocarbon groups but also those in which some of the hydrocarbon groups constitute the side chain of the skeleton.

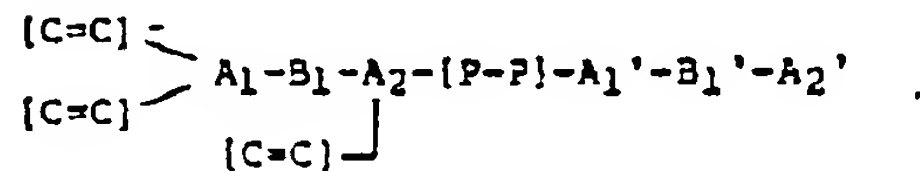
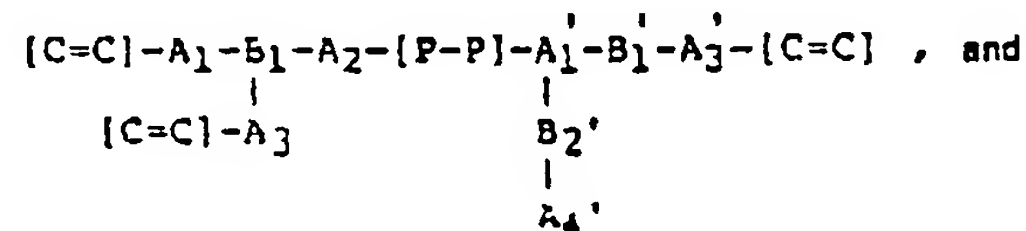
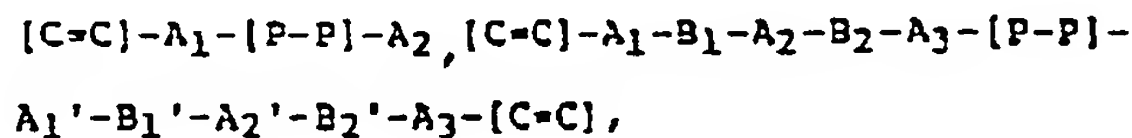
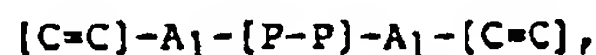
Illustrated below are the hydrocarbon groups (represented by A) connected through the linkage (represented by B) of



For simplicity, the group having the double bond is expressed by  $[C=C]$  and the



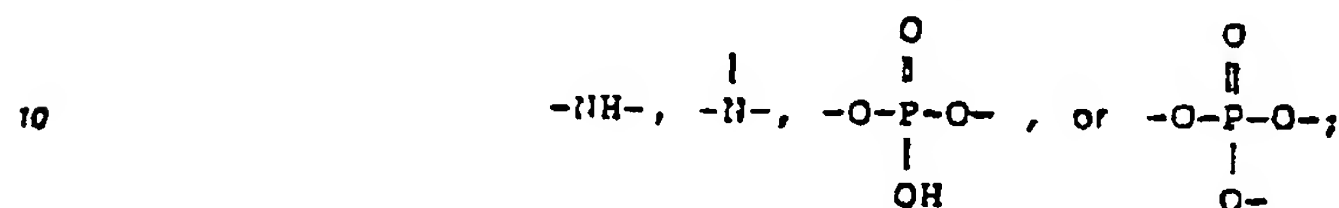
by [P-P] :



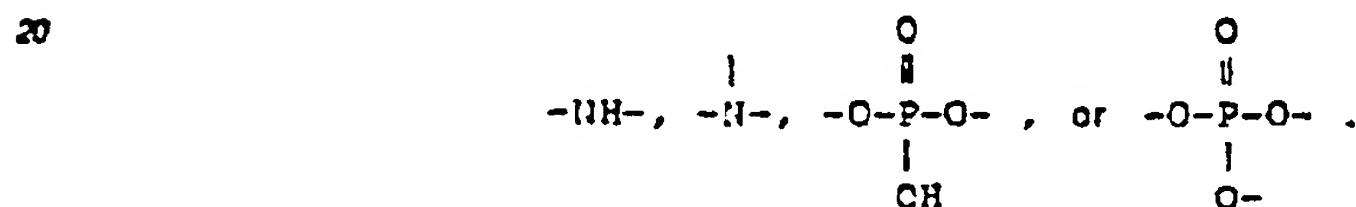
60 The term "hydrocarbon group" as used in this invention includes halogenated hydrocarbon groups, unless otherwise noted.

Among the compounds of the above formula, a pyrophosphate derivative of (meth)acrylic ester in which  $X_1$ ,  $X'_1$ ,  $X_2$ , and  $X'_2$  are oxygen and  $k$  and  $k'$  are 1 provides an adhesive which can be used in a variety of application areas. Particularly, those compounds in which  $R_1 = R'_1$ ,  $R_2 = R'_2$ , and  $m = n$  are easy to synthesize. Those compounds in which  $m = n = 1$  are preferable from the standpoint of adhesive strength. The preferred compound which exhibits high adhesive strength is one represented by formula

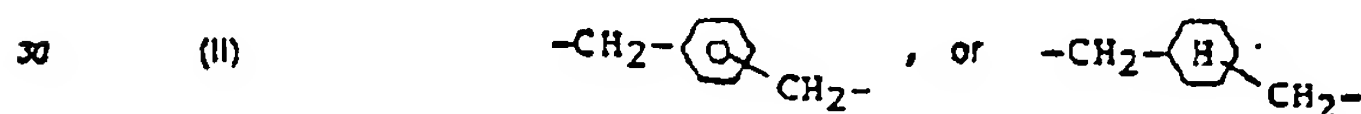
(I) in which  $R_1$  is (i) a  $C_{8-30}$  hydrocarbon group which may be substituted with a halogen, hydroxyl group, amino group, or carboxyl group, or (ii) a  $C_{2-30}$  hydrocarbon group in which 2 to 7 hydrocarbon groups [each of which may be substituted with a halogen, hydroxyl group, amino group, or carboxyl group and has 1 to 29 carbon atoms and at least one of them has 3 or more carbon atoms] are connected to one another through a linkage of the type of ether, thioether, ester, thioester, thiocarbonyl, amide, carbonyl, sulfonyl, urethane.



and  $R_2$  is (i) a  $C_{1-30}$  hydrocarbon group which may be substituted with a halogen, hydroxyl group, amino group, or carboxyl group, or (ii) a  $C_{2-30}$  hydrocarbon group in which 2 to 7 hydrocarbon groups [each of which may be substituted with a halogen, hydroxyl group, amino group, or carboxyl group and has 1 to 29 carbon atoms] are connected to one another through a linkage of the type of ether, thioether, ester, thioester, thiocarbonyl, amide, carbonyl, sulfonyl, urethane,



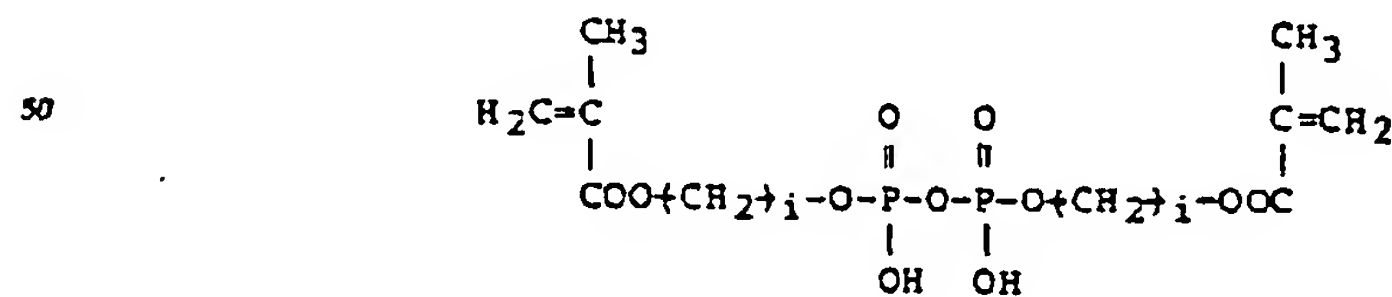
25 The particularly preferred structure of  $R_3$  is:  
(i)  $(-CH_2)_l$  [where  $l$  is an integer from 8 to 20.]



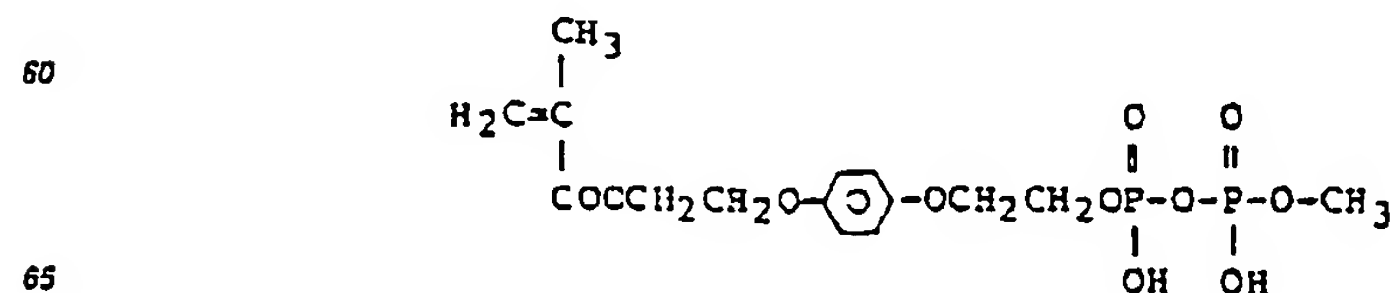
[where  $q$  is 2, 3, or 4.]



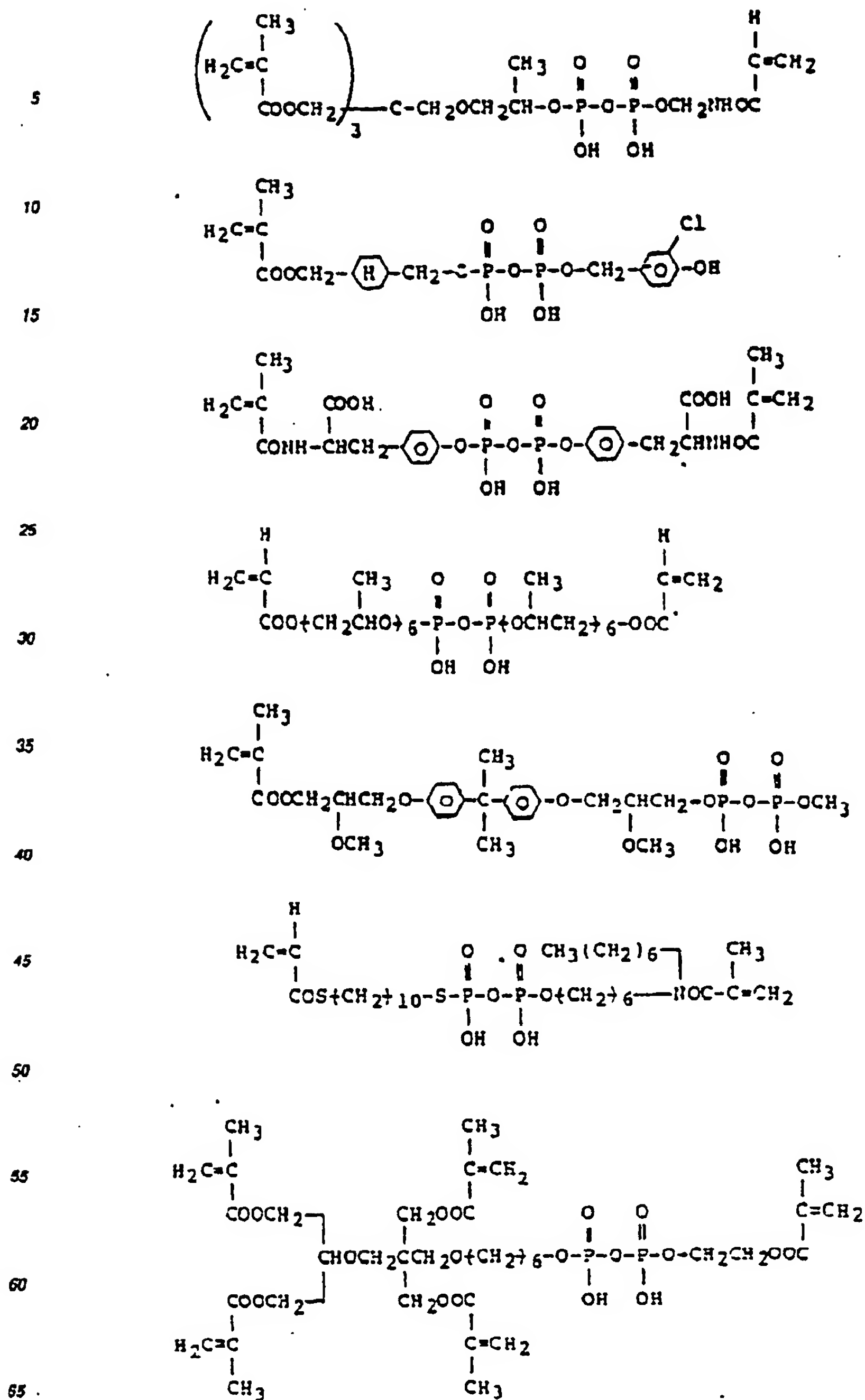
45 [where  $p$  is 0 or 1, and  $R_D$  is a  $C_{3-10}$  hydrocarbon group.]  
Examples of the adhesive monomer used in this invention are illustrated below.



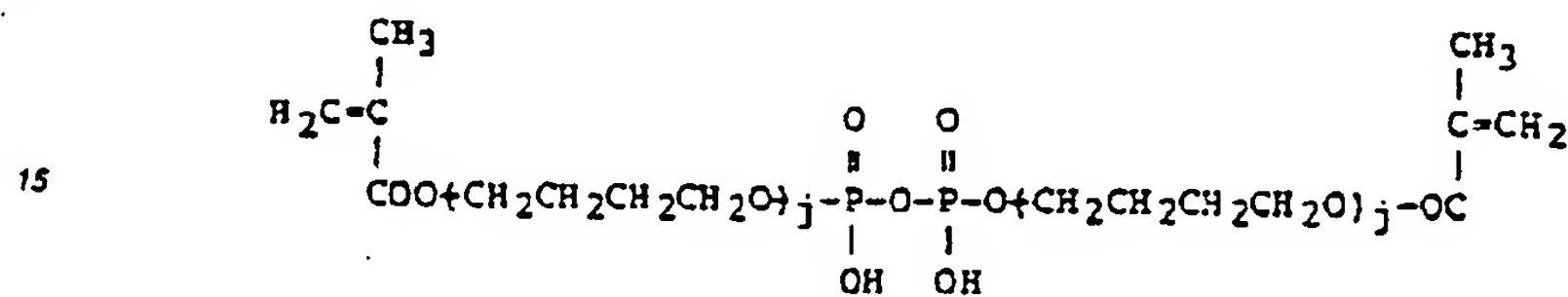
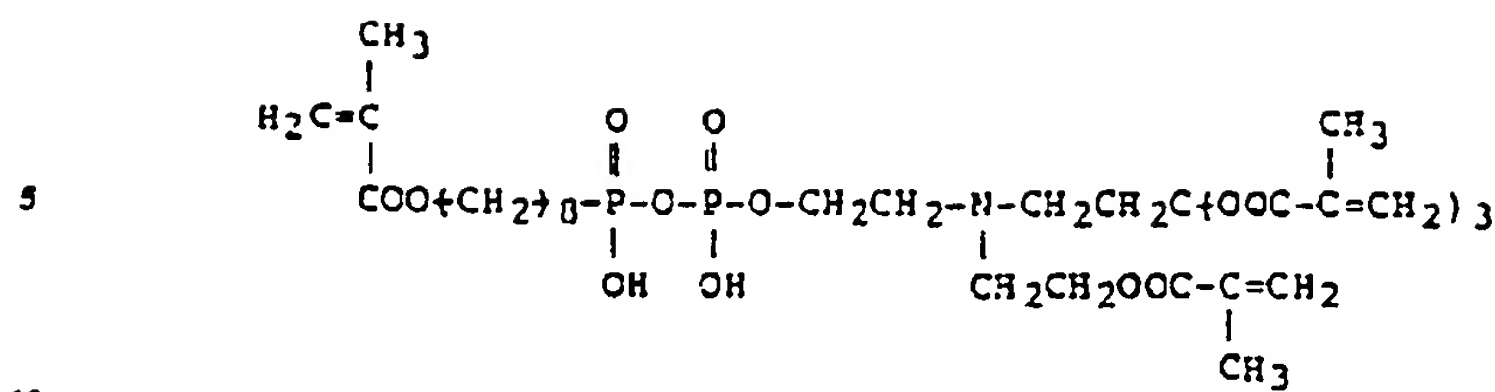
55 (where  $l = 8-20$ )



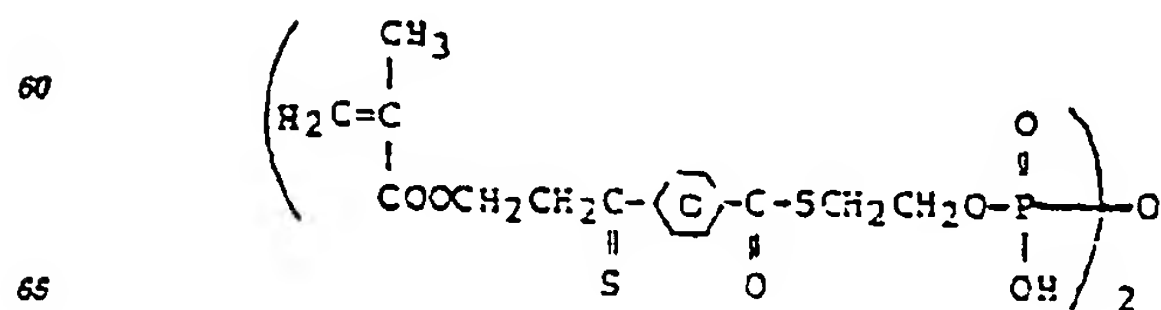
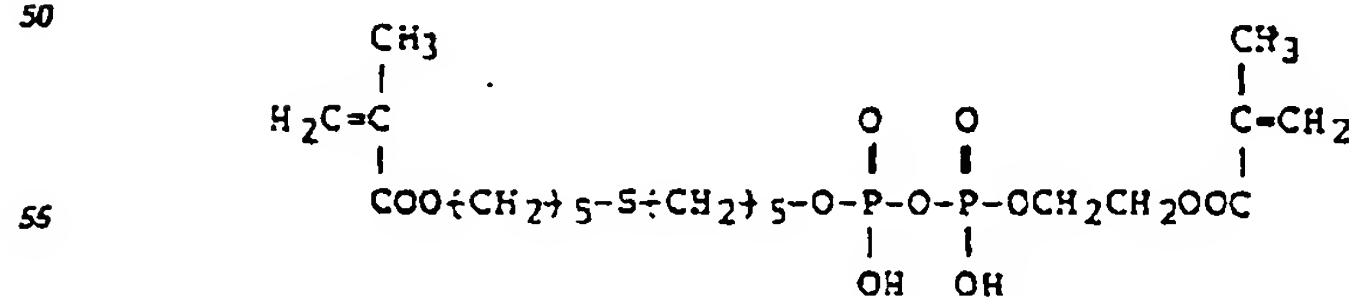
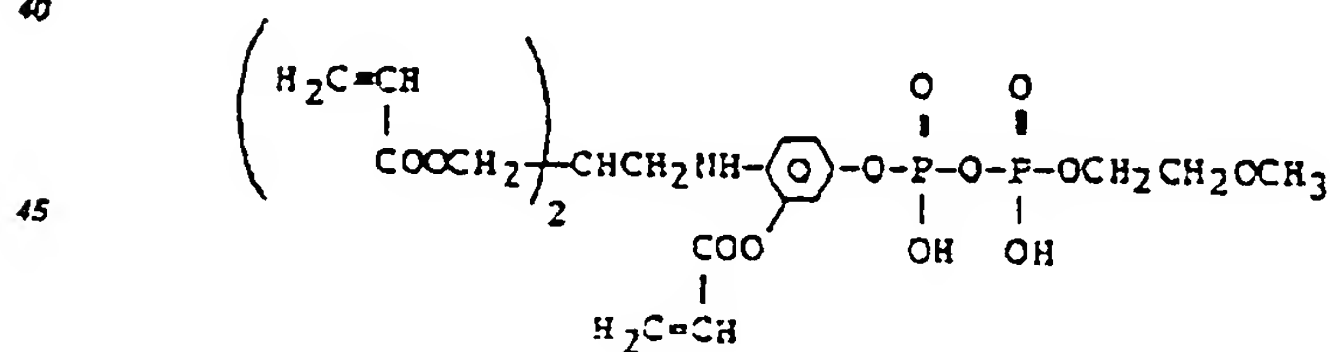
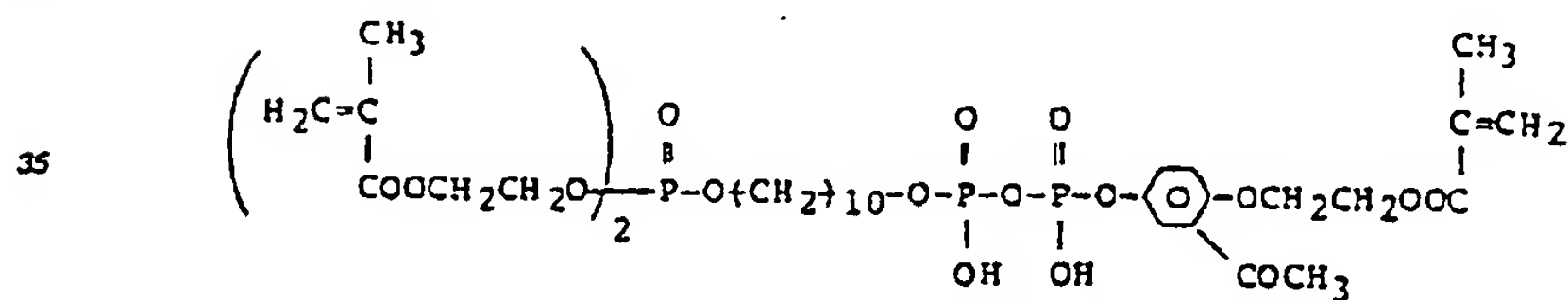
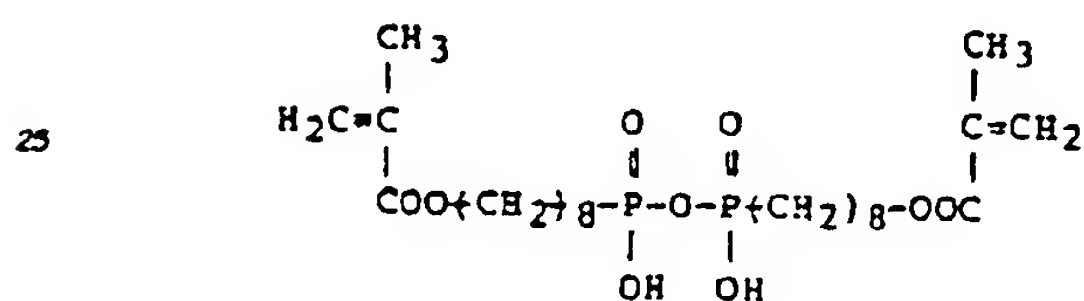
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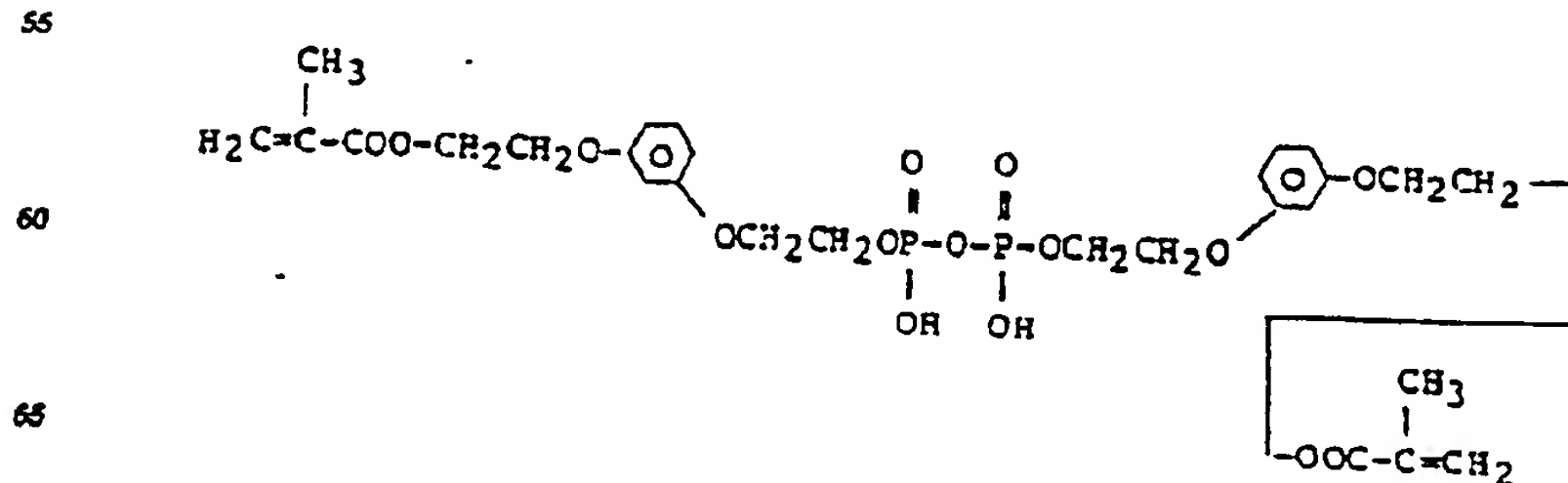
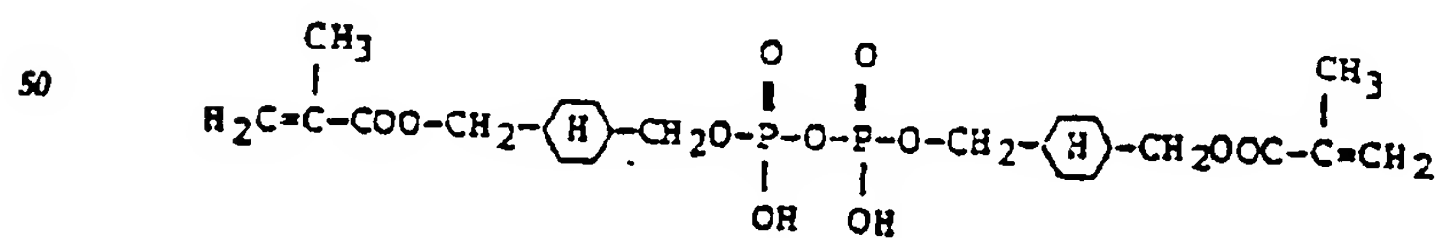
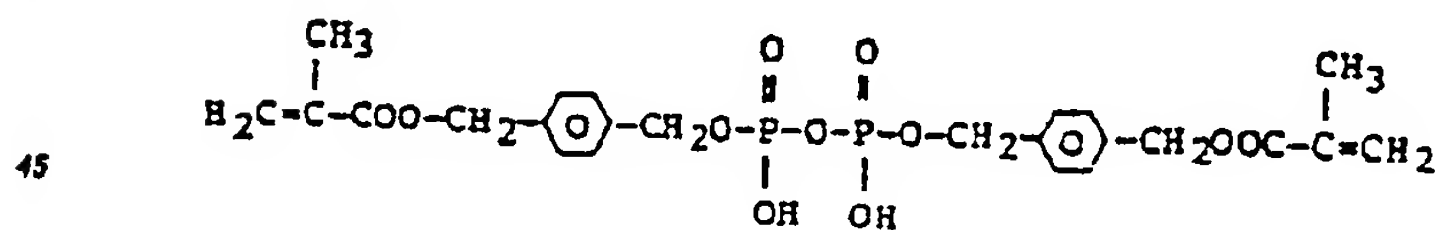
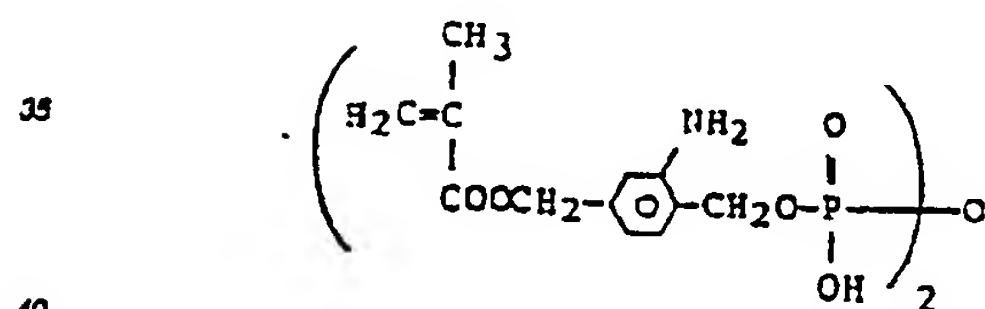
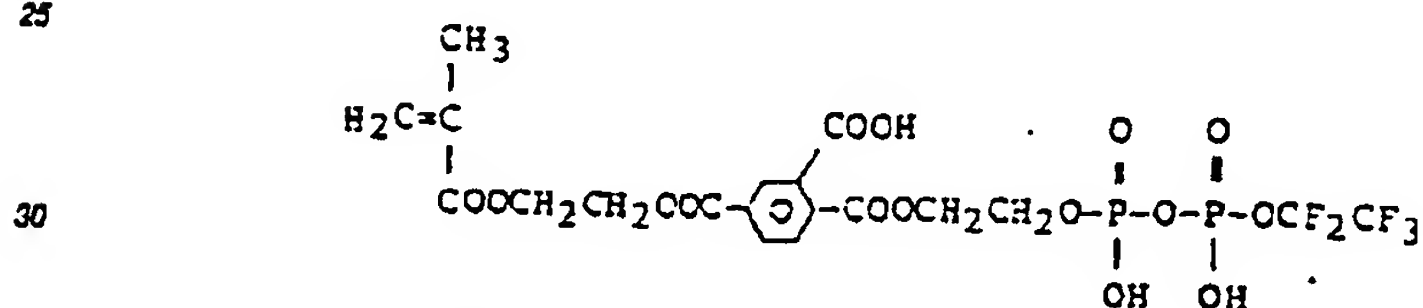
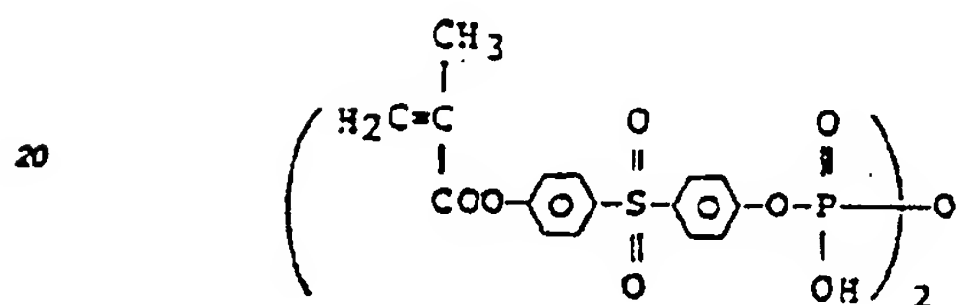
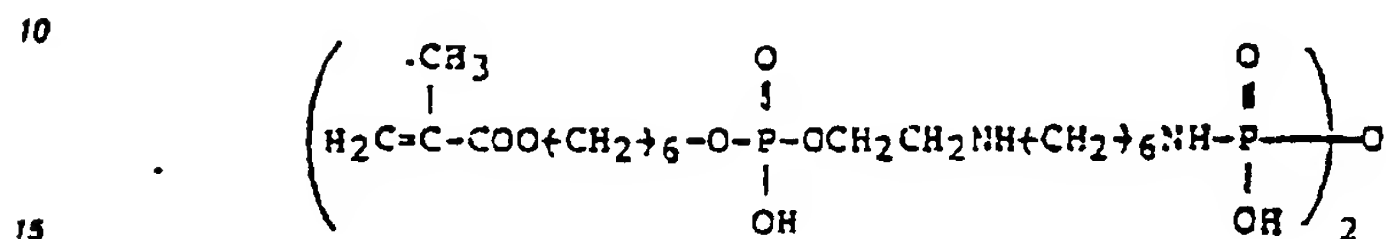
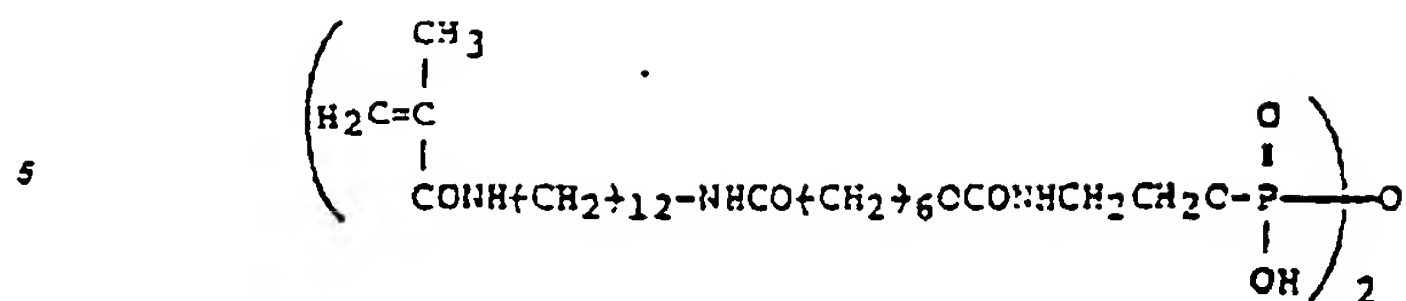
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(where J = 2-10)

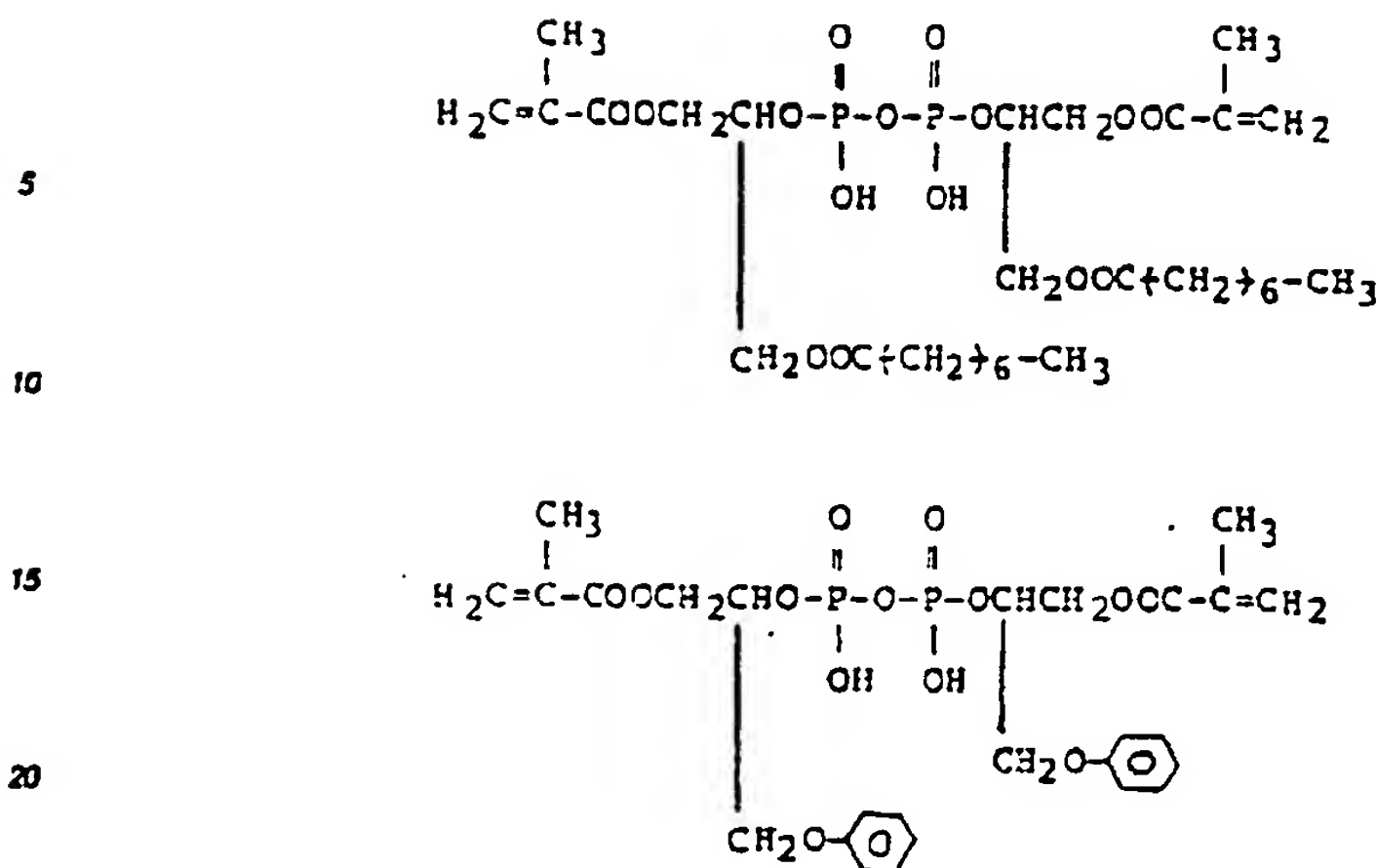






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25 When  $R_1$  in the compound of formula (I) contains seven or fewer carbon atoms, the resulting adhesive has extremely poor adhesion to teeth, metallic materials, and ceramics and the water resistance of its adhesive strength is also poor, as compared with the adhesive of this invention. In general, as the number of carbon atoms in  $R_1$  increases, the adhesive strength of the resulting adhesive tends to increase and then decrease. When  $R_1$  contains 8 to 40 and preferably 8 to 30 carbon atoms, the adhesive strength is sufficient to achieve the results of this invention. There is no lower limit to the number of carbon atoms in  $R_1$ ; but when  $R_1$  contains more than 40 carbon atoms, the resulting adhesive is poor in adhesive strength.

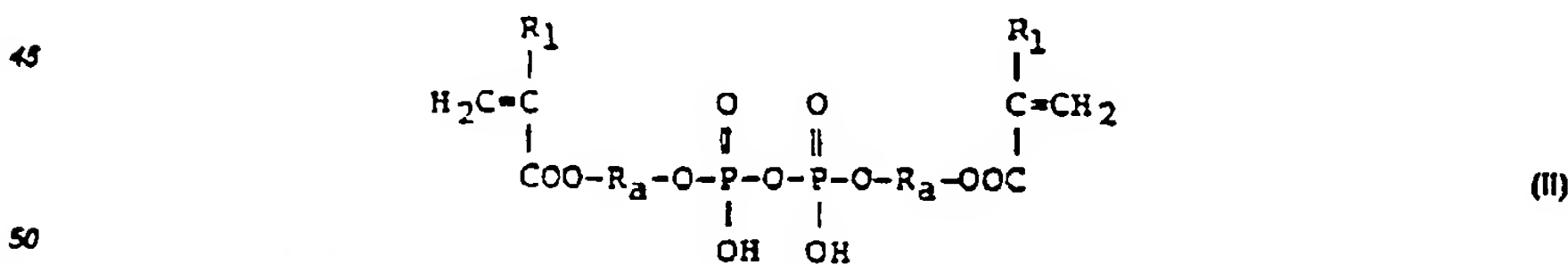
The compound of formula (I) can be synthesized according to the process for synthesizing phosphorus-containing compounds described in the following literature.

35 Organophosphorus Compounds, by G.M. Kosolapoff, published by Wiley, 1950.

Organophosphorus Monomers and Polymers, by Ye. L. Gelfer, published by Pergamon Press, 1962.

40 Modern Organic Synthesis Series 5, Organic phosphorus compounds, edited by The Society of Synthetic Chemistry, Japan, published by Gihodo, Bellstein (Springer-Verlag)

For example, the compound of the formula (I) wherein  $X_1$ ,  $X_1'$ ,  $X_2$ , and  $X_2'$  are oxygen;  $k$  and  $K$  are 1;  $R_1 = R_1'$ ,  $R_2 = R_2'$ , and  $m = n = 1$ , or the compound of the following formula (II)



is synthesized as follows:

At first,



is synthesized through the esterification reaction of (meth)acrylic acid and  $\text{HO}-R_2-\text{OH}$ . The compound

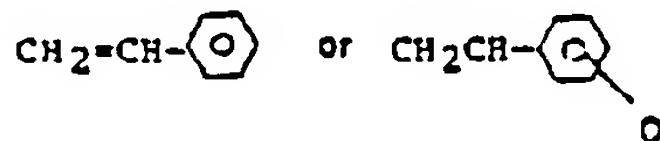
60 is changed into



by esterifying the OH group with  $\text{POCl}_3$  or pyrophosphoric acid. The phosphoric ester group is condensed by the dicyclohexylcarbodiimide process or by the dehydration with phosgene and pyridine. If  $\text{HO}-\text{R}_1-\text{OH}$  is replaced by  $\text{HS}-\text{R}_1-\text{SH}$ , it is possible to synthesize a compound of formula (II) in which O is replaced by S.

According to this invention, the adhesive (which may also be referred to as the adhesive composition) is prepared by mixing the compound of formula (I) with a vinyl monomer which is copolymerizable with the compound. The copolymerizable monomer affects the viscosity, wettability, curability, and mechanical properties of the adhesive. Thus it should be properly selected according to the intended use of the adhesive.

Usually, it is meth(acrylate) type monomer, styrene type monomer, or vinyl acetate. The monomer is not limited to them, however. It also includes (meth)acrylamide, N-n-butoxymethyl(meth)acrylamide, N-(hydroxymethyl)acrylamide, and other acrylamides; and (meth)acrylic acid, isobutylvinyl ether, diethyl fumarate, diethyl maleate, maleic anhydride, methyl vinyl ketone, allyl chloride, vinyl naphthalene, and vinylpyridine. The above-mentioned styrene type monomer includes those compounds (such as divinyl benzene and p-chlorostyrene) represented by



(where Q denotes a halogen or a  $\text{C}_{1-4}$  hydrocarbon group). The (meth)acrylate type monomer is one which is commonly used for anaerobic adhesives and dental adhesives. It is a (meth)acrylate monomer represented by



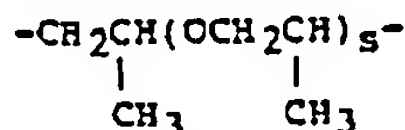
(where R<sub>1</sub> denotes H or CH<sub>3</sub>, U denotes a  $\text{C}_{1-30}$  organic group, t denotes an integer of 1 to 4, and the organic group is defined above). Examples of such monomers include the following.

(i) Monofunctional (meth)acrylate

Methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, decyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate (HEMA), 2-hydroxypropyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 3-chloro-2-hydroxypropyl methacrylate, and 2,3-dibromopropyl (meth)acrylate.

(ii) Difunctional (meth)acrylate

a) One in which U is  $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_s-$  or



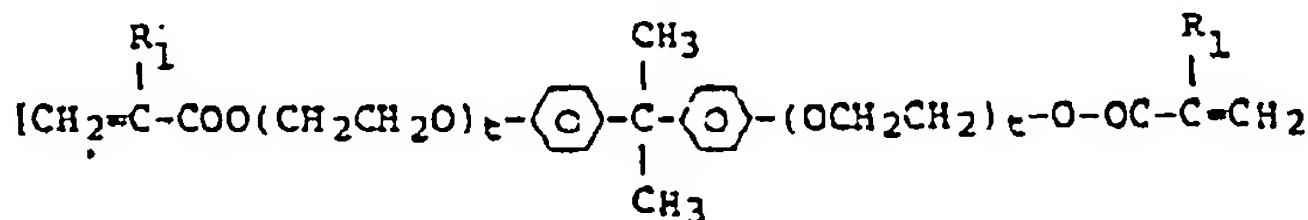
(where s is an integer of 0 to 15)

Ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, and tripropylene glycol di(meth)acrylate.

b) One in which U is an alkylene of carbon number 3 to 12

Propanediol di(meth)acrylate, glycerin di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,5-pentanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentylglycol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, and dibromoneopentyl glycol dimethacrylate.

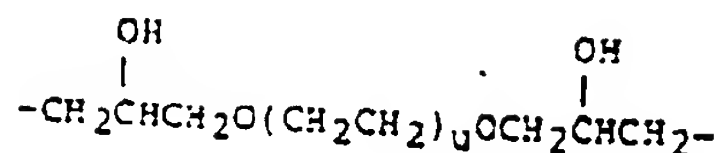
c) One in which U has a residue of bisphenol-A derivative Bisphenol-A di(meth)acrylate, 2,2-bis[4-(meth)acryloyloxy polyethoxyphenyl]propane.



where t is an integer of 1 to 9],

2,2-bis[4-(4-acryloyloxy propoxyphenyl)propane, and 2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane (Bis-GMA). Preferable among them are those in which U has a carbon number 15 to 30.

d) One in which U is



(where U is 1 or 2)

1,2-bis[3-(meth)acryloyloxy-2-hydroxypropoxy]ethane, and 1,4-bis[3-(meth)acryloyloxy-2-hydroxypropoxy]butane.

e) One in which U is JOCONHTNHCOOJ [where J denotes a C<sub>2-10</sub> alkylene, and T denotes an organic diisocyanate residue of carbon number 1 to 50].

Urethane di(meth)acrylate as disclosed in Japanese Patent Laid-open No. 687/1975.

(iii) Tri- and tetrafunctional methacrylates

Trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, and N,N'-(2,2,4-trimethylhexamethylene) bis [2-(aminocarboxy)propane-1,3-diol]tetramethacrylate.

The above-mentioned copolymerizable monomers are used individually or in combination with one another. The most preferred one for dental adhesive is methacrylate ester, and it should preferably account for more than 50 wt% of the total copolymerizable monomer. Preferred examples of methacrylate ester include methyl methacrylate, ethyl methacrylate, HEMA, n-hexyl methacrylate, benzyl methacrylate, lauryl methacrylate, bis-GMA, bisphenol-A dimethacrylate, 2,2-bis[(meth)acryloyloxy polyethoxyphenyl]propane, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, 1,8-hexanediol dimethacrylate, 1,10-decanediol dimethacrylate, neopentyl glycol dimethacrylate, are trimethylolethane trimethacrylate.

In the adhesive of this invention, the compound of formula (I) should be contained more than 0.5 wt% in the total polymerizable monomer; in other words, the above-mentioned copolymerizable monomer should be used in an amount of 1 to 199 parts by weight for 1 part by weight of the compound of formula (I). If the content of the compound of formula (I) is less than 0.5 wt%, the resulting adhesive is insufficient in adhesive strength. The amount of the compound of formula (I) is preferably more than 1.5 wt%.

The adhesive of this invention exhibits its adhesive strength when polymerized and cured after application to the adherend or filling into the cavity. The curing is accomplished physically with heating or irradiation of X-rays, ultraviolet rays, or visible light, or chemically with a polymerization initiator. Usually, the adhesive is incorporated with a photosensitizer or a polymerization initiator to facilitate curing. They are collectively called a curing agent in this invention. The curing agent that can be used in this invention includes organic peroxides, azo compounds, organometallic compounds, redox initiators, and photosensitizers for ultraviolet rays and visible light. Their examples include benzoyl peroxide, di-t-butyl peroxide, cumene hydroperoxide, t-butylhydroperoxide, methyl ethyl ketone peroxide, azobisisobutyronitrile, tributyl borane, organic sulfinic acid (or salt thereof), hydrogen peroxide/Fe<sup>2+</sup> salt, cumene hydroperoxide/Fe<sup>2+</sup> salt, benzoyl peroxide/N,N-dialkylaniline derivative, ascorbic acid/Cu<sup>2+</sup> salt, organic sulfinic acid (or salt thereof)/amine (or salt thereof)/peroxide, α-diketone/allylthiourea (visible light curing), benzoin methyl ether, benzoinethyl ether, benzyl, diacetyl, diphenyl-disulfide, and di-β-naphthyl sulfide. Preferable among them are benzoyl peroxide, azobisisobutyronitrile, tributyl borane, and organic sulfinic acid (or salt thereof)/diacyl peroxide/aromatic secondary or tertiary amine (or salt thereof). The aromatic sulfinic acid includes benzenesulfinic acid, p-toluenesulfinic acid, β-naphthalenesulfinic acid, and styrenesulfinic acid. The cation which forms a salt with the sulfinic acid is an alkali metal ion, alkaline earth metal ion, or ammonium ion. The former two are preferred from the standpoint of storage stability and adhesive strength. Their examples are Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup>. The preferred examples of aromatic amines include N,N-dimethylaniline, N,N-dimethyl-p-toluidine, N,N-diethylaniline, N,N-diethanolaniline, N-methylaniline, and N-methyl-p-toluidine. These amines may form a salt with hydrochloric acid, acetic acid, or phosphoric acid. The diacyl peroxide includes benzoyl peroxide, m-toluoyl-peroxide, 2,4-dichlorobenzoyl peroxide, octanoyl peroxide, lauroyl peroxide, and succinic acid peroxide. Preferable among them are benzoyl peroxide and m-toluoyl peroxide. These curing agents are added in an amount of 0.01 to 20 parts by weight, preferably 0.1 to 15 parts by weight, for 100 parts by weight of the polymerizable monomer.

In some cases, it is desirable to incorporate the adhesive of this invention with a volatile organic solvent having a boiling point lower than 150 °C at 760 Torr. Such an embodiment is preferable where the adhesive of this invention is used as a primer to be applied to the tooth cavity prior to the filling of a dental filling material. After application, the volatile organic solvent is vaporized by blowing air or nitrogen so that a film of the adhesive is formed on the adherend. The preferred organic solvent includes methanol, ethanol, acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, dichloromethane, chloroform, ethyl ether, isopropyl ether, and toluene. The volatile organic solvent is used in an amount of less than 300 times (by weight), preferably less than 100 times, the weight of the total polymerizable monomer. Dilution in excess of 300 times results in a great decrease in adhesive strength due to an excessively thin film of polymerizable monomer formed after the volatilization of the solvent.

The adhesive of this invention may be incorporated with a known filler (inorganic, organic polymer, or inorganic-organic composite type). When incorporated with a filler, the adhesive of this invention can be

used as a dental cement (for adhesion and filling), dental composite resin, and bone cement. The filler should be added in an amount of less than 1 000 parts by weight, preferably 20 to 500 parts by weight, for 100 parts by weight of the polymerizable monomer. The filler improves the rheological properties of the adhesive composition at the time of its use, the mechanical properties of the cured adhesive, and the adhesive strength and the resistance of the adhesive strength to water. Examples of the inorganic filler include natural minerals such as quartz, feldstone, pottery stone, wallastonite, mica, clay, kaolin, and marble; ceramics such as silica, alumina, silicon nitride, boron carbide, boron nitride, soda glass, barium glass, strontium glass, borosilicate glass, and lanthanum-containing glass ceramic; and water-insoluble inorganic salts such as barium sulfate and calcium carbonate. Usually, the inorganic filler undergoes surface treatment with a silane coupling agent such as  $\gamma$ -methacryloyloxypropyl trimethoxy silane, vinyl trimethoxy silane, vinyl triethoxy silane, vinyl trichlorosilane, vinyl tris(2-methoxyethoxy)silane, vinyl triacetoxy silane, and  $\gamma$ -mercaptopropyl trimethoxy silane. The organic polymeric filler includes polymethyl methacrylate, polyamide, polyester, polypeptide, polysulfone polycarbonate, polystyrene, chloroprene rubber, nitrile rubber, styrene-butadiene rubber, and polyvinyl acetate. The inorganic-organic composite type filler includes the silane-treated inorganic filler coated with the above-mentioned polymer.

These fillers are used individually or in combination with one another. The filler may be of formless, spherical, lamellar, or fibrous, having a particle diameter smaller than 100 microns. The polymeric filler may be dissolved in the polymerizable monomer or a volatile organic solvent. Inorganic fillers and inorganic-organic composite type fillers are preferable where the adhesive of this invention is used as a dental cement or dental composite resin, and organic fillers are preferable where it is used as a bone cement.

In the case where the adhesive of this invention is intended for industrial use and home use, the adhesive may be incorporated with an organic solvent-soluble polymer such as PMMA, polystyrene, polyvinyl acetate, chloroprene rubber, butadiene rubber, nitrile rubber, and chlorosulfonated polyethylene in an amount of less than 200 parts by weight, preferably less than 120 parts by weight, for 100 parts by weight of the vinyl monomer composition, whereby the adhesive is increased in viscosity and the mechanical properties of the cured adhesive are improved.

In addition to the above-mentioned additives, the adhesive of this invention may be incorporated with a polymerization inhibitor (e. g., hydroquinone methyl ether (MEHQ)), antioxidant (e. g., 2,6-di-tert-butyl-p-cresol (BHT)), ultraviolet absorbing agent, pigment, phthalic acid diester or silicone oil, as occasion demands, according to the performance required. These additives are added in an amount of less than 10 parts by weight, preferably less than 5 parts by weight, for 100 parts by weight of the polymerizable monomers.

In the case where the adhesive of this invention is used in the dentistry and orthopedics, a redox initiator of room temperature curing type is commonly used. In such a case, the oxidizing agent and the reducing agent should be packed separately to ensure storage stability, and a special attention should be paid to the package form. Examples of the package form include the two-pack systems, each pack containing vinyl compound plus reducing agent and vinyl compound plus oxidizing agent; vinyl compound plus oxidizing agent (or reducing agent) and volatile organic solvent plus reducing agent (or oxidizing agent); vinyl compound plus oxidizing agent (or reducing agent) and filler plus reducing agent (or oxidizing agent); or vinyl compound plus filler plus oxidizing agent and vinyl compound plus filler plus reducing agent. In the case of the three-component system composed of organic sulfinic acid (or salt thereof)/amine (or salt thereof)/peroxide, which is most suitable for the adhesive of this invention, the sulfinic acid and amine function as the reducing agent and the peroxide, as the oxidizing agent. In this case, a three-pack system may be employed in which the sulfinic acid and amine are separated from each other.

In the case where a photosensitizer is used as a curing agent, the package containing the vinyl compound and photosensitizer should be stored in a container shielded against light. In the case where an initiator (such as tributyl borane) is employed which initiates polymerization in a short time on contact with the vinyl compound, the initiator and the vinyl compound should be packed separately from each other. The two-pack adhesive composition is mixed together immediately before use.

The adhesive of this invention exhibits outstanding adhesion for a variety of materials as enumerated below, and keeps the high adhesive strength under a wet condition over a long period of time.

- (i) Hard tissues of the living body, such as teeth and bones.
- (ii) Base metals and alloys thereof such as iron, nickel, chromium, cobalt, aluminium, copper, zinc, tin, stainless steel, and brass; and noble metal alloys containing 50 to 90 % of gold or platinum, which are difficult to bond with a conventional adhesive.
- (iii) Ceramics such as glass, porcelain, silica, and alumina.
- (iv) Organic polymers such as polymethyl methacrylate, polyester, polyamide, polyurethane, polycarbonate, polysulfone, and polystyrene.

Because of its ability to exhibit high adhesive strength for a variety of materials as mentioned above, the adhesive of this invention will find use in various application areas. Examples of preferred applications are as follows:

- (i) Dentistry



The adhesive is applied to the wall of a tooth cavity to be filled with a composite resin which is usually composed of a polymerizable monomer, filler, and polymerization initiator. When supplied to the dentist, the adhesive is combined with the composite resin to form a system.

The adhesive composition incorporated with a filler is used as a composite resin to be filled in the tooth cavity. Not only does the adhesive composition function as a filling material but also it firmly adheres to the tooth.

The adhesive is used to bond an inlay, onlay, or abutment to a tooth cavity; to fasten a bridge, post, splint, or orthodontic bracket to teeth; or to bond a crown to an abutment.

The adhesive is used as a pit and fissure sealant.

For each application, the specific composition of the adhesive is selected as mentioned above. For example, if the adhesive is to be coated on a tooth prior to the filling of a composite resin, the adhesive composition may be prepared according to the recipe as shown in U.S. Patent Nos. 4,259,075 and 4,259,117. That is, the adhesive composition is made up of 1.5 to 100 wt% of the above-mentioned vinyl compound (which exhibits adhesion on polymerization), a polymerizable monomer (such as bis-GMA, HEMA, and aliphatic dimethacrylate), an organic solvent (such as ethanol) as a diluent, and a curing agent of room temperature curing type. Also, if the adhesive composition is to be used in the form of a composite resin, it is prepared according to the recipe shown in the above-mentioned U.S. Patents. That is, the above-mentioned adhesive vinyl compound is added in an amount of 1.5 to 50 wt% (based on the total polymerizable monomers) to a conventional filling material composed of 20 to 40 wt% of polymerizable monomer (such as bis-GMA) and 80 to 60 wt% of filler.

The adhesive thus prepared is applied to a tooth in the usual way. On curing, the composite resin adheres to a tooth so firmly that it is not necessary to provide mechanical retention such as undercut. (It is preferable to subject the tooth surface to acid etching before the adhesive of this invention is applied to the tooth; however, it provides practically sufficient adhesive strength without acid etching, unlike the compositions disclosed in U.S. Patent Nos. 4,259,075 and 4,259,117. There is some fear for the injurious effect of acid etching on the dentin).

The adhesive composition to bond an inlay, onlay, or crown to a tooth cavity or abutment should preferably be composed of 1.5 to 50 parts by weight of the adhesive vinyl monomer, 98.5 to 50 parts by weight of the copolymerizable monomer and 50 to 500 parts by weight of filler. With the adhesive composition thus prepared, it is possible to achieve the bonding of an inlay, onlay, or crown to a tooth cavity, which could not be achieved with a conventional luting cement.

In an additional application in the dentistry, a liquid composed of the adhesive vinyl monomer, copolymerizable monomer, and curing agent is applied to the tooth surface, followed by curing, so that the firmly-bonding film formed on the tooth surface prevents tooth decay.

#### (ii) Orthopedics

The adhesive composition of this invention will find use as a bone cement to bond a ceramic or metallic artificial joint or splint to a bone. The adhesive composition for such use should preferably be composed of 90 to 98.5 parts by weight of methyl methacrylate, 10 to 1.5 parts by weight of adhesive vinyl monomer, and 50 to 150 parts by weight of polymethyl methacrylate.

#### (iii) General industrial and home uses

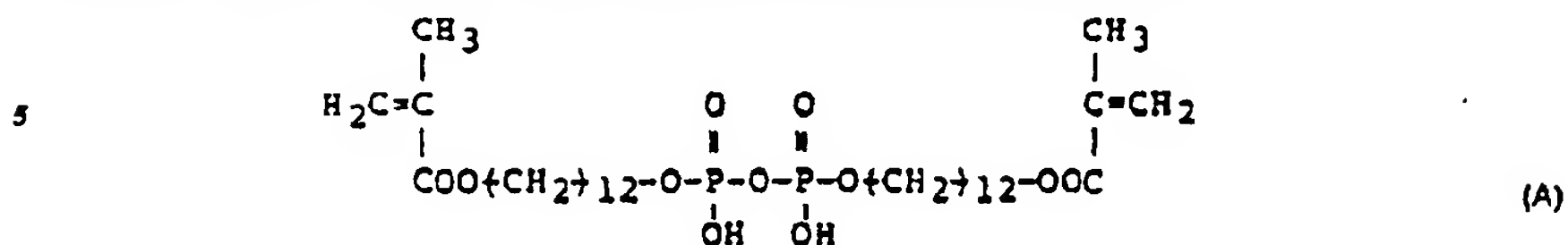
Because of its outstanding adhesion to metals, ceramics, and organic polymers, the adhesive of this invention will find general use in the areas of transport, electric machines, building materials, can manufacture, ceramic industry, and home appliances. It will also find use as coating materials such as a paint and an undercoating. When used for coating, it adheres much more firmly to the substrate than the existing adhesive of polymerization curing type (such as cyanoacrylate, epoxy resin, and second-generation acrylic adhesive), even if the substrate is stained with oil or wetted. This is a surprising feature of the adhesive of this invention.

Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are intended for purpose of illustration only and are not intended to be limiting.

#### Example 1

The adhesive monomer used in this invention was prepared as follows: A mixture of monomethacrylate ester and dimethacrylate ester of 1,12-dodecanediol was prepared by esterifying equimolar amounts of methacrylic acid and 1,12-dodecanediol at 90 °C in the presence of p-toluenesulfonic acid as a catalyst. After the determination of the molar ratio by high-speed liquid chromatography, the mixture was reacted at -50 °C with phosphorus oxychloride in an equimolar amount of the monoester. The remaining P-Cl bond was hydrolyzed at 0 °C to give a mixture of 12-methacryloxydodecyl dihydrogen phosphate and 1,12-dodecanediol dimethacrylate. After removal of dimethacrylate by extraction with n-hexane, there was obtained 12-methacryloyloxy dodecyl dihydrogen phosphate. 35 g of this phosphate and 10.3 g of dicyclohexylcarbodiimide were dissolved in 100 cc of ethyl acetate, followed by stirring at room temperature for 5 hours. The crystals of urea derivative which had separated out were filtered off. After adding 15 mg of BHT to the filtrate, the solvent was distilled away from the filtrate under reduced pressure to yield 33 g of nonvolatile residue. By elemental analysis and <sup>1</sup>H- and <sup>31</sup>P-NMR analyses, it was

confirmed that the residue is a pyrophosphate ester of the following formula.



A two-pack type primer was prepared from this compound according to the following recipe.

Formulation 1.

Parts by weight

Bis-GMA	50
HEMA	43
Compound (A)	7
Benzoyl peroxide	2

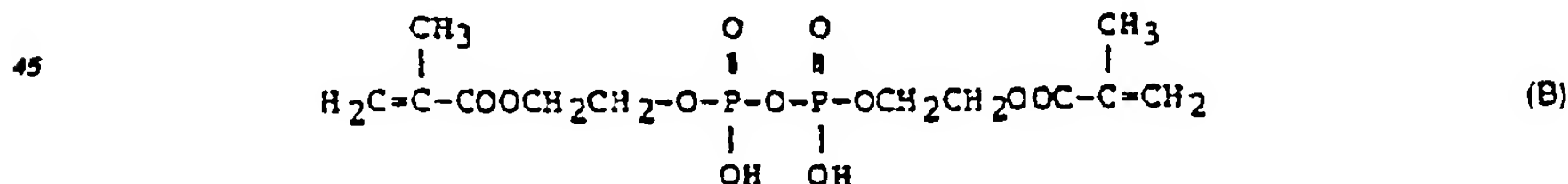
Formulation 2

Ethanol	100
Sodium benzenesulfonic acid	3
N,N-dimethyl-p-toluidine	0.7

A specimen for adhesion was prepared by embedding a human molar in an epoxy resin in a cylindrical holder and then cutting the crown so that the dentin was exposed. On the other hand, a stainless steel rod, measuring 7 mm in diameter and 25 mm long was provided. The surface of the dentin and the end of the stainless steel rod were polished with # 1 000 sand paper. The polished surface of the dentin was covered with a piece of adhesive tape having a hole 5 mm in diameter. This hole establishes the area of adhesion. Formulation 1 and formulation 2 were mixed in equal quantities, and the mixture was applied to the dentin surface and the end of the stainless steel rod. Immediately, air was blown to the coated surface by using an air syringe to vaporize ethanol. A commercial dental composite - Clearfil-F - was mixed and the resulting paste was cast up on the end of the stainless steel rod. The stainless steel rod was pressed against the surface of the dentin, with the paste interposed between the two surfaces. After being kept pressed for 30 minutes, the dentin specimen and the stainless steel rod which had been bonded together were dipped in water at 37 °C for one day. Tensile bonding strength was measured. The bonding strength was 66 kg/cm<sup>2</sup> when failure occurred at the dentin-composite resin interface.

Comparative example 1

Example 1 was repeated except that the compound (A) was replaced by a known pyrophosphate ester of the following formula (B).



The tensile bonding strength was 8 kg/cm<sup>2</sup>.

Example 2

As the adherends, round rods measuring 7 mm in diameter and 25 mm long were prepared from iron, aluminium, copper, nickel, porcelain, α-alumina, glass, polymethyl methacrylate, and polycarbonate. The end of each rod was polished with #1 000 silicon carbide sand paper. A 5 % ethanol solution of compound (A) was sparingly applied to each adherend, followed by evaporation of ethanol by an air syringe. A powder-liquid type adhesive prepared by mixing the following formulations in equal quantities was applied to the primed adherend. Two rods of the same kind were butted together.

Formulation 3.

Parts by weight

Methyl methacrylate	100
Benzoyl peroxide	1

## Formulation 4.

	Polymethyl methacrylate powder	100
	Sodium benzenesulfonate powder	3
5	N,N-diethanol-p-toluidine	1

After 1 hour, the bonded specimens were dipped in water at room temperature for 10 days. The tensile bonding strength was measured. The results are as follows :

10	Iron	351 kg/cm <sup>2</sup>
	Aluminium	298 kg/cm <sup>2</sup>
	Copper	256 kg/cm <sup>2</sup>
	Nickel	335 kg/cm <sup>2</sup>
	Porcelain	187 kg/cm <sup>2</sup>
15	$\alpha$ -Alumina	172 kg/cm <sup>2</sup>
	Glass	81 kg/cm <sup>2</sup>
	Polymethyl methacrylate	153 kg/cm <sup>2</sup>
	Polycarbonate	108 kg/cm <sup>2</sup>

## 20 Comparative Example 2

Example 2 was repeated except that compound (A) was replaced by compound (B). The bonding strength for iron, alumina, copper, nickel, porcelain,  $\alpha$ -alumina, and glass was lower than 50 kg/cm<sup>2</sup>.

## 25 Example 3

A powder-liquid type adhesive of the following composition was prepared from compound (A).

	Formulation 5.	Parts by weight
30	Bis-GMA	40
	HEMA	30
	Neopentylglycol dimethacrylate	20
	Compound (A)	10
35	Benzoyl peroxide	2
	MEHO	trace amount

## Formulation 6.

40	Silane-treated quartz powder	100
	Sodium benzenesulfonate powder	0.3
	N,N-diethanol-p-toluidine	0.4

45 An adherend specimen was prepared by embedding the crown of a bovine anterior tooth in an epoxy resin in a cylindrical holder, with the labial enamel surface exposed. After polishing with #1 000 sand paper, the enamel surface underwent acid etching with 40 % aqueous solution of orthophosphoric acid. After rinsing, the etched surface was dried by using an air syringe. On the other hand, there was provided a stainless steel round rod measuring 7 mm in diameter and 25 mm long, with the end polished with #1 000 sand paper.

50 A pasty adhesive was prepared by mixing 0.1 g of formulation 5 and 0.3 g of formulation 6. The adhesive was applied to the end of the round stainless steel rod. The end of the rod was pressed against the etched surface. After being kept pressed for 1 hour, the specimens were dipped in water at 37 °C for 1 day. The tensile bonding strength was measured. The bonding strength was 205 kg/cm<sup>2</sup> when failure occurred at the enamel — adhesive interface.

55

## Examples 4 to 9

Adhesives were prepared from the compounds listed in Table 1 according to Example 1, and their bonding strength for human tooth dentin was evaluated. In addition, a powder-liquid type adhesive was prepared in the same way as in Example 3 except that compound (A) was replaced by the compounds in Table 1. Their bonding strength for an Ni-Cr alloy was evaluated.

60 A dental Ni-Cr alloy [Now Chrom (I), made by Towa Giken K.K.] was cast into a square plate measuring 4 × 10 × 10 mm. The 10 × 10 mm surface of the alloy plate was polished with #1 000 sand paper. The polished surface was covered with a piece of adhesive tape having a hole 5 mm in diameter. This hole  
65 establishes the area of bonding. On the other hand, a stainless steel round rod measuring 7 mm in



diameter and 30 mm long was provided. The end of the rod was polished by sandblasting with alumina abrasive having an average particle diameter of 33 microns at a pressure of 3.5 kg/cm<sup>2</sup>. A paste obtained by mixing 0.3 g of adhesive powder and 0.1 g of adhesive liquid was applied to the end of the stainless steel round rod. The end of the stainless steel rod was pressed against the Ni-Cr alloy plate. After being kept pressed for 1 hour, the specimens were dipped in water at 37 °C for 1 day. The tensile bonding strength was measured on an Instron tensile tester (at a crosshead speed of 2 mm/min).

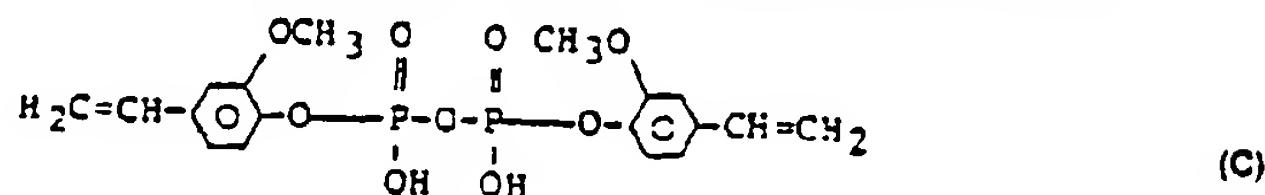
The results are shown in Table 1.

Table 1

Example	Compound	Bonding strength (kg/cm <sup>2</sup> )	
		Human tooth	Ni-Cr alloy
4	$\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COO}-(\text{CH}_2)_9-\text{O}-\text{P} \begin{array}{c} \text{O} \\    \\ \text{OH} \end{array} \end{array} \right)_2-\text{O}$	67	325
5	$\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{O}-\text{P} \begin{array}{c} \text{O} \\    \\ \text{OH} \end{array} \end{array} \right)_2-\text{O}$	58	298
6	$\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{O}-\text{P} \begin{array}{c} \text{O} \\    \\ \text{OH} \end{array} \end{array} \right)_2-\text{O}$	58	262
7	$\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2-\text{O}-\text{P} \begin{array}{c} \text{O} \\    \\ \text{OH} \end{array} \end{array} \right)_2-\text{O}$	64	320
8	$\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2\text{CH} \begin{array}{c}   \\ \text{CH}_2\text{OOC}-(\text{CH}_2)_6-\text{CH}_3 \end{array} \end{array} \right)_2-\text{O}-\text{P} \begin{array}{c} \text{O} \\    \\ \text{OH} \end{array}$	52	253
9	$\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{COOCH}_2\text{CH} \begin{array}{c}   \\ \text{CH}_2-\text{O}-\text{C}_6\text{H}_4 \end{array} \end{array} \right)_2-\text{O}-\text{P} \begin{array}{c} \text{O} \\    \\ \text{OH} \end{array}$	54	306

## Comparative Example 3

Adhesives were prepared according to Examples 4 to 9 from a compound of formula (C).



10 Their bonding strength for the human tooth dentin and an Ni-Cr alloy (Now Chrom (I), made by Towa Giken K.K.) was 11 kg/cm<sup>2</sup> and 33 kg/cm<sup>2</sup>, respectively. These results are apparently inferior to those in Table 1.

## Example 10

15 A cylindrical cavity measuring 4 mm in diameter and 4 mm deep was formed on the lingual surface of a human molar by using a diamond burr. The cavity was dried by using an air syringe. A mixture of equal quantities of formulation 1 and formulation 2 in Example 1 was applied to the entire cavity wall. Air was blown to the coated surface by using an air syringe to vaporize ethanol. A commercial dental composite resin - Clearfil-F - was filled in the cavity in the usual way. The tooth specimen was dipped in water at 37 °C for 1 day. Then, the tooth specimen was dipped in water at 4 °C and water at 60 °C alternately 100 times for 1 minute each. The water was colored with a dye. The tooth specimen was cut with a cutter to see if the dye had infiltrated into the interface between the tooth and the filler. The infiltration of the dye was not found at all.

## Example 11

25 A conical cavity measuring 6 mm in diameter and 4 mm deep was formed on the occlusal surface of a human molar. An inlay that fits in the cavity was cast from type III gold alloy. A 1 : 3.0 mixture (by weight) of formulation 5 and formulation 6 in Example 3 was applied to the conical surface of the inlay. The inlay was forced into the cavity to effect bonding. After 30 minutes, the tooth specimen was dipped in water at 37 °C for 1 day. Then, the tooth specimen was subjected to thermal cycling test by dipping in water at 4 °C and water at 60 °C alternately 100 times. After the test, the inlay stayed in the cavity so firmly that it could not be pried off by a knife tip.

## Example 12

35 A 1 mm thick plate that fits to the lingual surface of a human anterior tooth was prepared by casting from an Ni-Cr alloy (Ni : 78 %, Cr : 12 %, Mo : 3 %, others : 9 %). The surface of the casting that comes into contact with the tooth was polished by sandblasting with 33 micron alumina abrasive. The lingual surface of the anterior tooth underwent acid etching for 1 minute with 40 % aqueous solution of phosphoric acid. A 1 : 3.0 mixture (by weight) of formulation 5 and formulation 6 in Example 3 was applied to the surface of the casting. The casting was bonded to the lingual surface of the anterior tooth. After 10 minutes, the bonded specimens were dipped in water at 37 °C for 1 day. The tensile bonding strength was 183 kg/cm<sup>2</sup>. Interfacial failure occurred at the tooth surface.

## Example 13

50 A pit and fissure sealant for filling the fissure of a molar was prepared according to the following composition.

Formulation 7.		Parts by weight
2,2-Bis(methacryloyloxypolyethoxyphenyl) propane		60
Neopentylglycol dimethacrylate		20
Compound (A)		10
HEMA		10
Benzoyl peroxide		2
60 Formulation 8.		
Bis-GMA		
HEMA		40
Neopentylglycol dimethacrylate		40
Sodium benzenesulfinate		20
65 N,N-diethanol-p-toluidine		2
		2

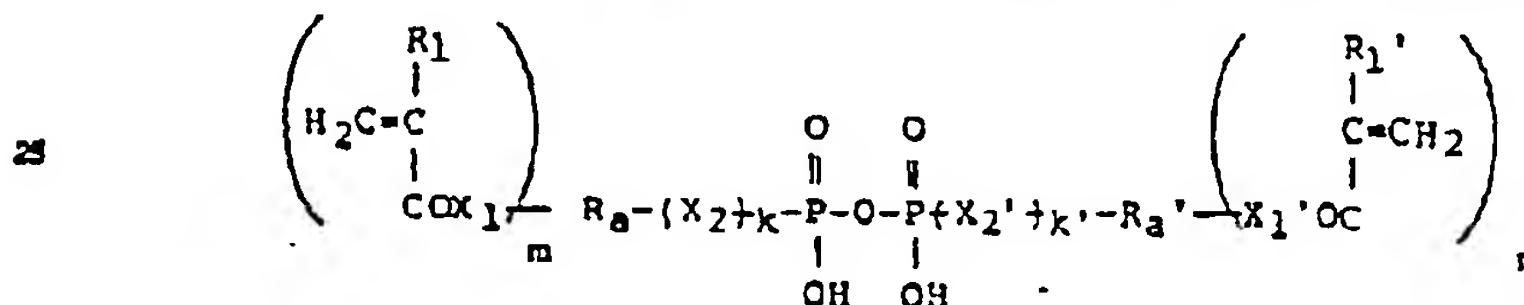
The fissure of a human molar was cleaned with an explorer, followed by washing and drying. The sealant (a 1 : 1 mixture of formulation 7 and formulation 8) was filled in the fissure without etching. Ten minutes after curing, the tooth specimen was dipped in water at 37 °C for 1 day. Then, the tooth specimen was dipped in water at 4 °C and water at 80 °C alternately 100 times for 1 minute each. The water was colored with a dye. The tooth specimen was cut with a cutter to see if the dye had infiltrated into the interface between the tooth and the filling material. The infiltration of the dye was hardly found.

## Example 14

A cylindrical cavity measuring 4 mm in diameter and 4 mm deep was formed on the buccal surface of a human molar by using a diamond burr. The cavity wall underwent acid etching for 1 minute with 40 % aqueous solution of phosphoric acid, followed by washing and drying. The paste obtained by mixing formulation 5 and formulation 8 in Example 3 in the ratio of 1 : 3.0 by weight was filled in the cavity. Ten minutes after curing, the tooth specimen was dipped in water at 37 °C for 1 day. Then, the heat-cycle test was conducted as in Example 13. The infiltration of dye into the interface was hardly found.

## Claims

1. An adhesive comprising (a) 1 part by weight of a compound represented by the formula



in which each

$R_1$  and  $R_1'$  is a hydrogen atom or a methyl group, each of  $X_1$ ,  $X_1'$ ,  $X_2$  is O, S, or  $NR^*$ , where  $R^*$  is a hydrogen atom or a  $C_{1-4}$  alkyl group.

$m$  is 1, 2, 3 or 4,

$n$  is 0, 1, 2, 3 or 4, each of

$k$  and  $k'$  is 0 or 1,

$R_a$  is a  $C_{8-20}$  organic residue having a valency of  $(m+1)$ , and

$R_a'$  is a  $C_{1-20}$  organic residue having a valency of  $(n+1)$ ; and

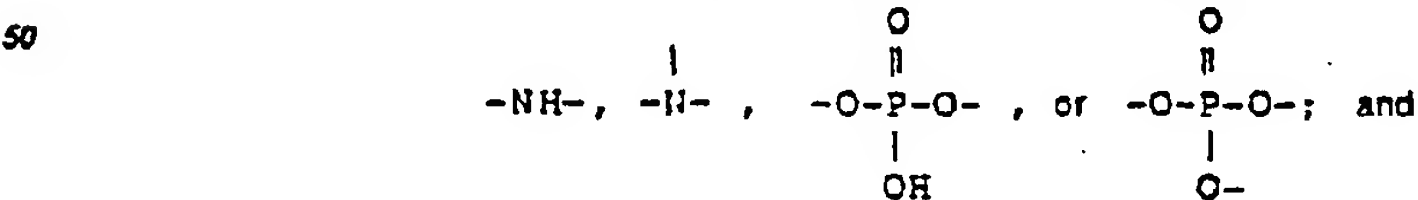
(b) 0 to 199 parts by weight of a monomer that is copolymerizable with the compound (I).

2. An adhesive as claimed in Claim 1, in which all of  $X_1$ ,  $X_1'$ ,  $X_2$ , and  $X_2'$  are oxygen, and  $k$  and  $k'$  are both 1.

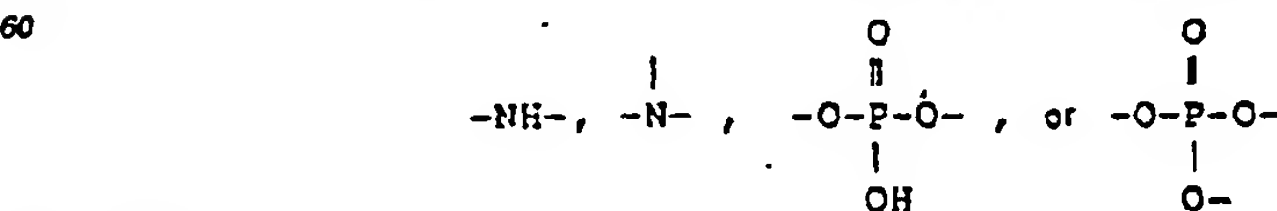
3. An adhesive as set forth in Claim 1 or 2, in which  $R_a'$  is identical with  $R_a$ ,  $R_1'$  is identical with  $R_1$ , and  $n = m$ .

4. An adhesive as claimed in Claim 3, in which  $m$  and  $n$  are both 1.

5. An adhesive as claimed in any preceding claim, in which  $R_a$  is (i) a  $C_{8-20}$  hydrocarbon group, optionally having halogen, hydroxy, amino or carboxy substitution or (ii) a  $C_{1-20}$  hydrocarbon group in which from two to seven  $C_{1-20}$  hydrocarbon groups, at least one of which has 3 or more carbon atoms, that optionally have halogen, hydroxy, amino or carboxyl substitution, are connected to one another through an ether, thioether, ester, thioester, thiocarbonyl, amide, carbonyl, sulfonyl, urethane,

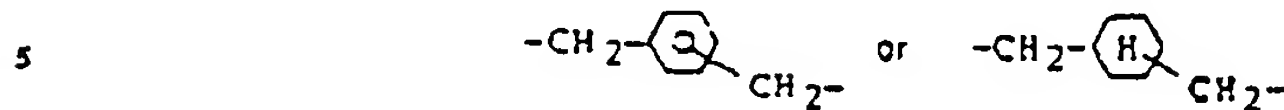


$R_a'$  is (i) a  $C_{1-20}$  hydrocarbon group, optionally having halogen, hydroxy, amino or carboxy substitution, or (ii) a  $C_{1-20}$  hydrocarbon group in which from two to seven  $C_{1-20}$  hydrocarbon groups optionally having halogen, hydroxy, amino or carboxy substitution are connected to one another through an ether, thioether, ester, thioester, thiocarbonyl, amide, carbonyl, sulfonyl, urethane,

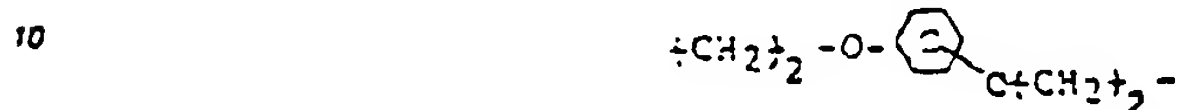


linkage.

6. An adhesive as claimed in Claim 4, in which  $R_2$  is  $-(CH_2)_n-$ , where  $n$  is an integer from 8 to 20.  
 7. An adhesive as claimed in Claim 4, in which  $R_2$  is



8. An adhesive as claimed in Claim 4, in which  $R_2$  is



where  $q$  is 2, 3, or 4.

9. An adhesive as claimed in Claim 4, in which  $R_2$  is



20 where  $p$  is 0 or 1 and  $R_3$  is a  $C_{1-18}$  hydrocarbon group.

10. An adhesive as claimed in Claim 1, in which the vinyl monomer (b) is a (meth)acrylate ester type monomer, styrene type monomer, or vinyl acetate.

11. An adhesive as claimed in any preceding claim that also includes 0.01 to 20 parts by weight of a curing agent per 100 parts by weight of the polymerizable monomers (a) + (b).

- 25 12. An adhesive as claimed in Claim 11, in which the curing agent is a polymerization initiator of the redox type.

13. An adhesive as claimed in Claim 12 in multipack form, in which the oxidizing and reducing components of the redox initiator are in separate packs.

14. An adhesive as claimed in Claim 11, in which the curing agent is a photosensitizer.

- 30 15. An adhesive as claimed in Claim 14 in two-pack form, in which the initiator and the vinyl compound are in separate packs.

16. An adhesive as claimed in any preceding claim that also includes less than 300 parts by weight of a volatile organic solvent having a boiling point lower than  $150^\circ\text{C}$  at 760 Torr (1 013 Pa) per part by weight of the polymerizable monomers (a) + (b).

- 35 17. An adhesive as claimed in any preceding claim that also includes 20 to 500 parts by weight of a filler per 100 parts by weight of the polymerizable monomers (a) + (b).

18. A dental adhesive as claimed in any one of Claims 11 to 15 or as claimed in Claim 16 as dependent on any one of Claims 11 to 15, for use in filling into a tooth cavity.

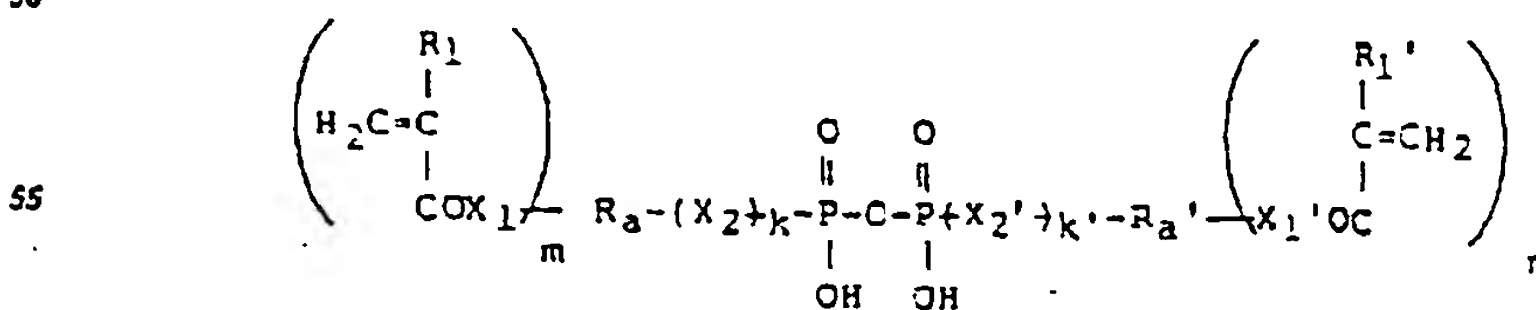
- 40 19. A dental adhesive as claimed in Claim 17 as appendant to any one of Claims 11 to 15, for use in filling into a tooth cavity.

20. A dental adhesive as claimed in Claim 17 as dependent on any one of Claims 11 to 15, for use in bonding between a tooth and a dental restorative material or between dental restorative materials.

21. A dental adhesive as claimed in any one of Claims 11 to 15 for use in coating a tooth surface for prevention of dental caries.

#### Patentansprüche

1. Klebstoff aus (a) 1 Gew.-Teil einer Verbindung der Formel



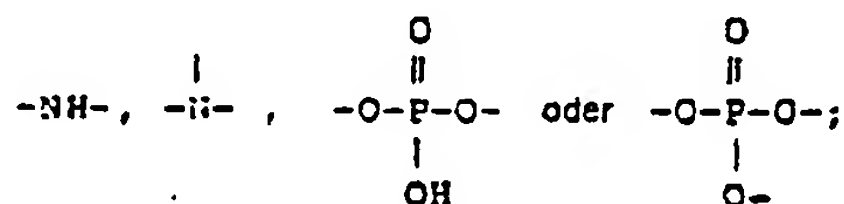
60 worin jeweils  $R_1$  und  $R_1'$  ein Wasserstoffatom oder eine Methylgruppe sind, jeweils  $X_1$ ,  $X_1'$ ,  $X_2$  und  $X_2'$  O, S oder  $NR^*$  sind, wobei  $R^*$  ein Wasserstoffatom oder eine  $C_{1-6}$ -Alkylgruppe ist,  $m$  1, 2, 3 oder 4 ist,  $n$  0, 1, 2, 3 oder 4 ist, jeweils  $k$  und  $k'$  0 oder 1 sind,  $R_2$  ein  $C_{1-40}$ -organischer Rest mit einer Wertigkeit von  $(m+1)$  ist und  $R_2'$  ein  $C_{1-40}$ -organischer Rest mit einer Wertigkeit von  $(n+1)$  ist, und (b) 0 bis 199 Gew.-Teilen eines Monomeren, das mit der Verbindung (I) copolymerisierbar ist.

2. Klebstoff nach Anspruch 1, dadurch gekennzeichnet, daß alle Substituenten  $X_1$ ,  $X_1'$ ,  $X_2$  und  $X_2'$  Sauerstoff sind, und  $k$  und  $k'$  jeweils 1 sind.

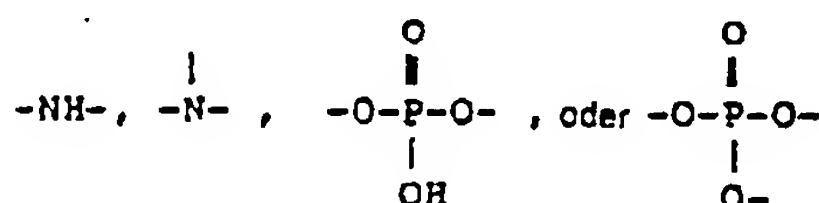
3. Klebstoff nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß  $R_1$  identisch ist mit  $R_2$ ,  $R_1$  identisch ist mit  $R_3$  und  $n = m$ .

4. Klebstoff nach Anspruch 3, dadurch gekennzeichnet, daß  $m$  und  $n$  jeweils 1 sind.

5. Klebstoff nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß  $R_1$  (i) eine  $C_{1-20}$ -Kohlenwasserstoffgruppe ist, die gegebenenfalls eine Halogen-, Hydroxy-, Amino- oder Carboxysubstitution aufweist, oder (ii) eine  $C_{1-20}$ -Kohlenwasserstoffgruppe ist, in welcher zwei bis sieben  $C_{1-20}$ -Kohlenwasserstoffgruppen, wobei wenigstens eine davon drei oder mehr Kohlenstoffatome aufweist, die gegebenenfalls eine Halogen-, Hydroxy-, Amino- oder Carboxylsubstitution aufweisen können, miteinander über eine Äther-, Thioäther-, Ester-, Thioester-, Thiocarbonyl-, Amid-, Carbonyl-, Sulfonyl-, Urethan-



Verknüpfung verbunden sind, und  $R_1$  (i) eine  $C_{1-20}$ -Kohlenwasserstoffgruppe ist, die gegebenenfalls eine Halogen-, Hydroxy-, Amino- oder Carboxysubstitution aufweist, oder (ii) eine  $C_{1-20}$ -Kohlenwasserstoffgruppe ist, in der zwei bis sieben  $C_{1-20}$ -Kohlenwasserstoffgruppen, die gegebenenfalls eine Halogen-, Hydroxy-, Amino- oder Carboxysubstitution aufweisen, miteinander über eine Äther-, Thioäther-, Ester-, Thioester-, Thiocarbonyl-, Amid-, Carbonyl-, Sulfonyl-, Urethan-



Verknüpfung verbunden sind.

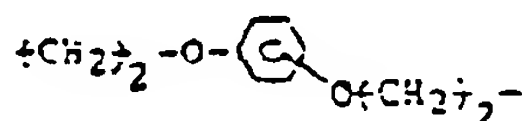
6. Klebstoff nach Anspruch 4, dadurch gekennzeichnet, daß  $R_1$   $-(CH_2)_n-$  bedeutet, wobei  $n$  eine ganze Zahl von 8 bis 20 ist.

7. Klebstoff nach Anspruch 4, dadurch gekennzeichnet, daß  $R_1$



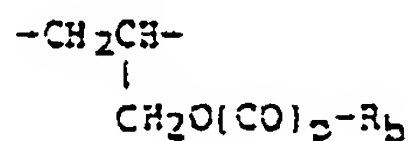
ist.

8. Klebstoff nach Anspruch 4, dadurch gekennzeichnet, daß  $R_1$



wobei  $q$  2, 3 oder 4 bedeutet, ist.

9. Klebstoff nach Anspruch 4, dadurch gekennzeichnet, daß  $R_1$



ist, wobei  $p$  0 oder 1 ist und  $R_2$  eine  $C_{1-10}$ -Kohlenwasserstoffgruppe ist.

10. Klebstoff nach Anspruch 1, dadurch gekennzeichnet, daß das Vinylmonomere (b) ein (Meth) Acrylatestermonomeres, Styrolmonomeres oder Vinylacetat ist.

11. Klebstoff nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß er auch 0,01 bis 20 Gew.-Teile eines Härtungsmittels pro 100 Gew.-Teile der polymerisierbaren Monomeren (a) - (b) enthält.

12. Klebstoff nach Anspruch 11, dadurch gekennzeichnet, daß das Härtungsmittel ein Polymerisationsinitiator des Redoxtyps ist.

13. Klebstoff nach Anspruch 12 in einer Verpackung, in welcher die oxidierenden und reduzierenden Komponenten des Redoxinitiators in getrennten Packungen vorliegen.

14. Klebstoff nach Anspruch 11, wobei das Härtungsmittel ein Photosensibilisator ist.

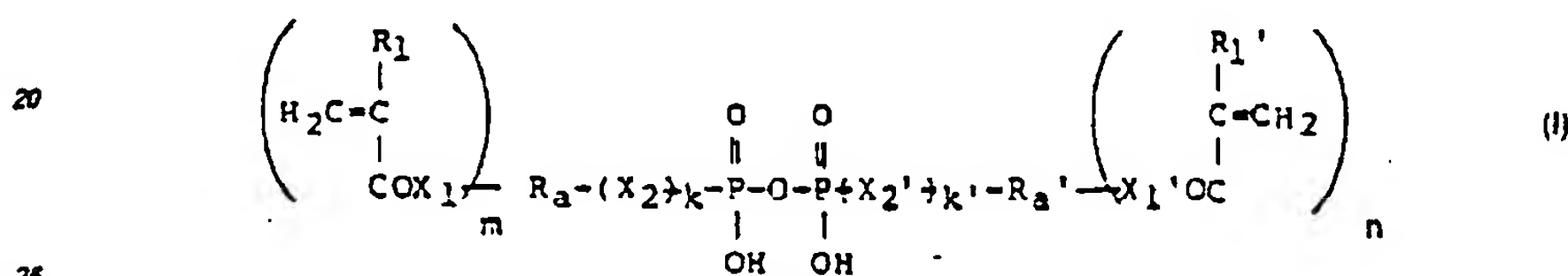
15. Klebstoff nach Anspruch 14 in einer Zweipackungsform, wobei der Initiator und die Vinylverbindung in getrennten Packungen vorliegen.

16. Klebstoff nach einem der vorhergehenden Ansprüche, der auch weniger als 300 Gew.-Teile eines flüchtigen organischen Lösungsmittels mit einem Siedepunkt von weniger als 150 °C bei 760 Torr (1 013 Pa) pro Gew.-Teil der polymerisierbaren Monomeren (a) - (b) enthält.

17. Klebstoff nach einem der vorhergehenden Ansprüche, der auch 20 bis 500 Gew.-Teile eines Füllstoffs pro 100 Gew.-Teile der polymerisierbaren Monomeren (a) + (b) enthält.
18. Zahnklebstoff nach einem der Ansprüche 11 bis 15 oder nach Anspruch 16 in Abhängigkeit von einem der Ansprüche 11 bis 15 für eine Verwendung zum Einfüllen in eine Zahnkavität.
19. Zahnklebstoff nach Anspruch 17 in Abhängigkeit von einem der Ansprüche 11 bis 15 für eine Verwendung zum Einfüllen in eine Zahnkavität.
20. Zahnklebstoff nach Anspruch 17 in Abhängigkeit von einem der Ansprüche 11 bis 15 für eine Verwendung in einer Bindung zwischen einem Zahn und einem Zahnreparaturmaterial oder zwischen Zahnreparaturmaterialien.
21. Zahnklebstoff nach einem der Ansprüche 11 bis 15 für eine Verwendung in einem Überzug einer Zahnoberfläche zur Verhinderung einer Zahnkaries.

# Revendications

1. Un adhésif comprenant (a) une partie en poids d'un composé représenté par la formule



dans laquelle chaque

$R_1$  et  $R'$  est un atome d'hydrogène ou un groupe méthyle, chacune de  $X_1$ ,  $X'$ ,  $X_2$  et  $X_2'$  est O, S ou  $NR^*$  où  $R^*$  est un atome d'hydrogène ou un groupe alcoyle en  $C_{1-6}$ .

$m$  est 1, 2, 3 ou 4

$n$  est 0, 1, 2, 3 ou 4, chacun de

$k$  et  $k'$  est 0 ou 1.

$R_a$  est un reste organique en  $C_{1-20}$  ayant une valence de  $(m+1)$  et

$R_a'$  est un reste organique en  $C_{1-20}$  ayant une valence de  $(n+1)$ ; et

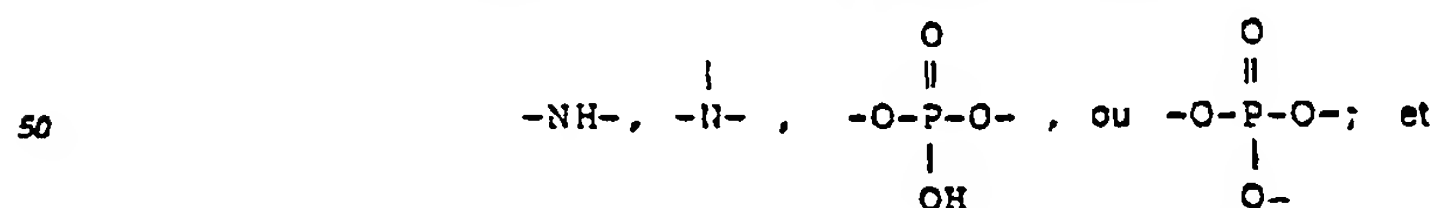
(b) 0 à 199 parties en poids d'un monomère qui est copolymérisable avec le composé (I).

2. Un adhésif comme revendiqué dans la revendication 1 dans lequel  $X_1$ ,  $X_1'$ ,  $X_2$  et  $X_2'$  sont tous un oxygène et  $k$  et  $k'$  sont tous deux 1.

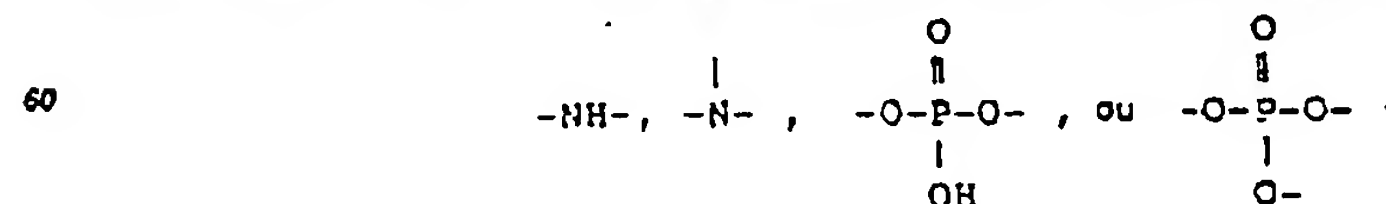
3. Un adhésif comme indiqué dans la revendication 1 ou 2 où  $R_a'$  est identique à  $R_a$ ,  $R_1'$  est identique à  $R_1$ , et  $n = m$ .

4. Un adhésif comme revendiqué dans la revendication 3 dans lequel  $m$  et  $n$  sont tous deux 1.

5. Un adhésif comme revendiqué dans l'une quelconque des revendications précédentes où  $R_a$  est (i) un groupe hydrocarboné en  $C_{1-30}$  ayant éventuellement une substitution halogène, hydroxy, amino ou carboxy ou (ii) un groupe hydrocarboné en  $C_{1-30}$  dans lequel 2 à 7 groupes hydrocarbonés en  $C_{1-20}$  dont au moins 1 à 3 atomes de carbone ou plus, qui éventuellement ont une substitution halogène, hydroxy, amino ou carboxyle, sont raccordés entre eux par un éther, un thioéther, un ester, un thioester, un thiocarbonyle, un amide, un carboxyle, un sulfonyle, un uréthane

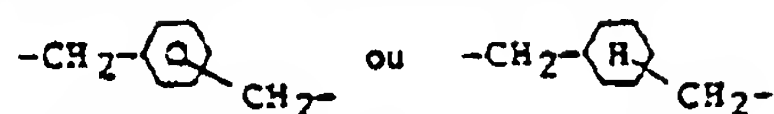


$R_a'$  est (i) un groupe hydrocarboné en  $C_{1-30}$  ayant éventuellement une substitution halogène, hydroxy, amino ou carboxy, ou (ii) un groupe hydrocarboné en  $C_{1-30}$  dont 2 à 7 groupes hydrocarbonés en  $C_{1-20}$  ayant éventuellement une substitution halogène, hydroxy, amino ou carboxy sont réunis entre eux par une liaison éther, thioéther, ester, thioester, thiocarbonyle, amide, carbonyle, sulfonyle, uréthane

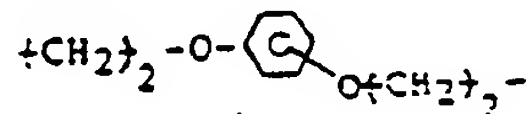


6. Un adhésif comme revendiqué dans la revendication 4 où  $R_a$  est  $-(CH_2)_n-$ , où  $n$  est un entier de 8 à 20.

7. Un adhésif comme revendiqué dans la revendication 4 où  $R_1$  est

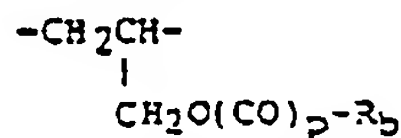


8. Un adhésif comme revendiqué dans la revendication 4 où  $R_1$  est



où q est 2, 3 ou 4.

9. Un adhésif comme revendiqué dans la revendication 4 où  $R_1$  est



où p est 0 et 1 et  $R_2$  est un groupe hydrocarboné en  $\text{C}_{3-18}$ .

10. Un adhésif comme revendiqué dans la revendication 1 dans lequel le monomère vinylique (b) est un monomère de type ester de type (méth)acrylate, un monomère de type styrène ou l'acétate de vinyle.

11. Un adhésif comme revendiqué dans l'une quelconque des revendications précédentes qui comprend aussi 0,01 à 20 parties en poids d'un agent de durcissement pour 100 parties en poids des monomères polymérisables (a) + (b).

12. Un adhésif comme revendiqué dans la revendication 11 dans lequel l'agent de durcissement est un amorceur de polymérisation du type redox.

13. Un adhésif comme revendiqué dans la revendication 12 sous forme d'un emballage multiple dans lequel les composants oxydant et réducteur de l'amorceur redox sont dans des emballages séparés.

14. Un adhésif comme revendiqué dans la revendication 11 dans lequel l'agent de durcissement est un photosensibilisateur.

15. Un adhésif comme revendiqué dans la revendication 14 sous forme d'un emballage double dans lequel l'amorceur et le composé vinylique sont dans des emballages séparés.

16. Un adhésif comme revendiqué dans l'une quelconque des revendications précédentes qui comprend également moins de 300 parties en poids d'un solvant organique volatil ayant un point d'ébullition inférieur à 150 °C à 750 torrs (1 013 Pa) par partie en poids des monomères polymérisables (a) + (b).

17. Un adhésif comme revendiqué dans l'une quelconque des revendications précédentes qui comprend aussi 20 à 500 parties en poids d'une charge pour 100 parties en poids des monomères polymérisables (a) + (b).

18. Un adhésif dentaire comme revendiqué dans l'une quelconque des revendications 11 à 15 ou comme revendiqué dans la revendication 16 dans la mesure où elle est rattachée à l'une quelconque des revendications 11 à 15 pour l'emploi dans l'obturation d'une cavité dentaire.

19. Un adhésif dentaire comme revendiqué dans la revendication 17 dans la mesure où elle est rattachée à l'une quelconque des revendications 11 à 15 pour l'emploi dans l'obturation d'une cavité dentaire.

20. Un adhésif dentaire comme revendiqué dans la revendication 17 dans la mesure où elle est rattachée à l'une quelconque des revendications 11 à 15 pour l'emploi dans l'union d'une dent et d'un matériau de restauration dentaire ou de matériaux de restauration dentaire entre eux.

21. Un adhésif dentaire comme revendiqué dans l'une quelconque des revendications 11 à 15 pour l'emploi dans le revêtement d'une surface dentaire pour la prévention des caries dentaires.